

ELEMENTARY QUANTITATIVE ANALYSIS

Theory and Practice

Second Edition

W. J. Blaedel and V. W. Meloche

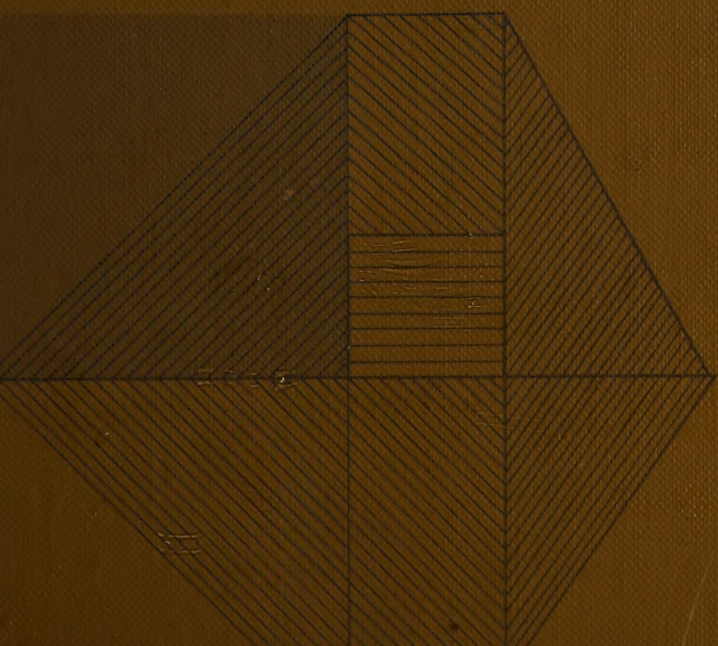


Table of Atomic Weights, 1961 * (Based on Carbon-12)

	Sym- bol	Atomic Number	Atomic Weight		Sym- bol	Atomic Number	Atomic Weight
Actinium	Ac	89		Mercury	Hg	80	200.59
Aluminum	Al	13	26.9815	Molybdenum	Mo	42	95.94
Americium	Am	95		Neodymium	Nd	60	144.24
Antimony	Sb	51	121.75	Neon	Ne	10	20.183
Argon	Ar	18	39.948	Neptunium	Np	93	
Arsenic	As	33	74.9216	Nickel	Ni	28	58.71
Astatine	At	85		Niobium	Nb	41	92.906
Barium	Ba	56	137.34	Nitrogen	N	7	14.0067
Berkelium	Bk	97		Nobelium	No	102	
Beryllium	Be	4	9.0122	Osmium	Os	76	190.2
Bismuth	Bi	83	208.980	Oxygen	O	8	15.9994†
Boron	B	5	10.811†	Palladium	Pd	46	106.4
Bromine	Br	35	79.909†	Phosphorus	P	15	30.9738
Cadmium	Cd	48	112.40	Platinum	Pt	78	195.09
Calcium	Ca	20	40.08	Plutonium	Pu	94	
Californium	Cf	98		Polonium	Po	84	
Carbon	C	6	12.01115†	Potassium	K	19	39.102
Cerium	Ce	58	140.12	Praseodymium	Pr	59	140.907
Cesium	Cs	55	132.905	Promethium	Pm	61	
Chlorine	Cl	17	35.453†	Protactinium	Pa	91	
Chromium	Cr	24	51.996†	Radium	Ra	88	
Cobalt	Co	27	58.9332	Radon	Rn	86	
Copper	Cu	29	63.54	Rhenium	Re	75	186.2
Curium	Cm	96		Rhodium	Rh	45	102.905
Dysprosium	Dy	66	162.50	Rubidium	Rb	37	85.47
Einsteinium	Es	99		Ruthenium	Ru	44	101.07
Erbium	Er	68	167.26	Samarium	Sm	62	150.35
Europium	Eu	63	151.96	Scandium	Sc	21	44.956
Fermium	Fm	100		Selenium	Se	34	78.96
Fluorine	F	9	18.9984	Silicon	Si	14	28.086†
Francium	Fr	87		Silver	Ag	47	107.870†
Gadolinium	Gd	64	157.25	Sodium	Na	11	22.9898
Gallium	Ga	31	69.72	Strontium	Sr	38	87.62
Germanium	Ge	32	72.59	Sulfur	S	16	32.064†
Gold	Au	79	196.967	Tantalum	Ta	73	180.948
Hafnium	Hf	72	178.49	Technetium	Tc	43	
Helium	He	2	4.0026	Tellurium	Te	52	127.60
Holmium	Ho	67	164.930	Terbium	Tb	65	158.924
Hydrogen	H	1	1.00797†	Thallium	Tl	81	204.37
Indium	In	49	114.82	Thorium	Th	90	232.038
Iodine	I	53	126.9044	Thulium	Tm	69	168.934
Iridium	Ir	77	192.2	Tin	Sn	50	118.69
Iron	Fe	26	55.847†	Titanium	Ti	22	47.90
Krypton	Kr	36	83.80	Tungsten	W	74	183.85
Lanthanum	La	57	138.91	Uranium	U	92	238.03
Lead	Pb	82	207.19	Vanadium	V	23	50.942
Lithium	Li	3	6.939	Xenon	Xe	54	131.30
Lutetium	Lu	71	174.97	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.312	Yttrium	Y	39	88.905
Manganese	Mn	25	54.9380	Zinc	Zn	30	65.37
Mendelevium	Md	101		Zirconium	Zr	40	91.22

* Reprinted by permission of the International Union of Pure and Applied Chemistry and Butterworths Scientific Publications.

† The atomic weight varies because of natural variations in the isotopic composition of the element. The observed ranges are boron, ± 0.003 ; carbon, ± 0.00005 ; hydrogen, ± 0.00001 ; oxygen, ± 0.0001 ; silicon, ± 0.001 ; sulfur, ± 0.003 .

‡ The atomic weight is believed to have an experimental uncertainty of the following magnitude: bromine, ± 0.002 ; chlorine, ± 0.001 ; chromium, ± 0.001 ; iron, ± 0.003 ; silver, ± 0.003 . For other elements the last digit given is believed to be reliable to ± 0.5 .

Formula Weights of Common Radicals *

AsO ₃	122.92	CrO ₄	115.99	PO ₄	94.97
AsO ₄	138.92	Cr ₂ O ₇	215.99	P ₂ O ₇	173.94
BrO ₃	127.91	Fe(CN) ₆	211.96	PtCl ₆	407.80
BrO ₄	143.91	IO ₃	174.90	SO ₃	80.06
CO ₃	60.01	IO ₄	190.90	SO ₄	96.06
C ₂ O ₄	88.02	MnO ₄	118.94	S ₂ O ₃	112.13
CN	26.018	MoO ₄	159.94	S ₂ O ₈	192.12
CHO ₂ , formate	45.018	NH ₄ ⁺	18.039	SCN	58.08
C ₂ H ₃ O ₂ , acetate	59.05	NO ₂	46.006	SiO ₃	76.08
ClO ₃	83.45	NO ₃	62.00	UO ₂	270.03
ClO ₄	99.45	OH	17.007		

Formula Weights of Common Substances *

AgBr	187.78	HC ₄ H ₇ O ₂ N ₂ , di-methylglyoxime	116.12	MoO ₃	143.94
AgCl	143.32	HC ₇ H ₅ O ₂ , benzoic acid	122.12	Na ₂ B ₄ O ₇ · 10H ₂ O	381.37
AgI	234.77	HC ₉ H ₆ ON, 8-hydroxy-quinoline	145.16	NaBr	102.90
AgNO ₃	169.88	HNH ₂ SO ₃ , sulfamic acid	97.09	Na ₂ CO ₃	105.99
Al ₂ O ₃	101.96	H ₂ O	18.015	Na ₂ C ₂ O ₄	134.00
As ₂ O ₃	197.84	H ₂ O ₂	34.015	NaCl	58.44
As ₂ S ₃	246.04	HgCl ₂	271.50	Na ₂ H ₂ C ₁₀ H ₁₂ O ₈ N ₂ · 2H ₂ O, EDTA, disodium salt	372.24
B ₂ O ₃	69.62	HgO	216.59	Na ₂ O	61.98
BaCO ₃	197.35	HgS	232.65	NaOH	39.997
BaCl ₂	208.25	KBr	119.01	Na ₂ SO ₄	142.04
BaCrO ₄	253.33	KBrO ₃	167.01	Na ₂ S ₂ O ₃	158.11
Ba(NO ₃) ₂	261.35	K ₂ CO ₃	138.21	NH ₃	17.031
BaO	153.34	KCl	74.56	(NH ₄) ₂ C ₂ O ₄	124.10
BaSO ₄	233.40	KClO ₃	122.55	(NH ₄) ₂ Ce(NO ₃) ₆	548.23
BeO	25.012	KClO ₄	138.55	(NH ₄) ₂ SO ₄	132.14
Bi ₂ O ₃	465.96	K ₂ CrO ₄	194.20	Ni(C ₄ H ₇ O ₂ N ₂) ₂ , Ni dimethylglyoxime	288.94
CO ₂	44.011	K ₂ Cr ₂ O ₇	294.19	NiO	74.71
CaCO ₃	100.09	KHC ₈ H ₄ O ₄ , KHP	204.23	P ₂ O ₅	141.94
CaC ₂ O ₄	128.10	KI	166.01	P ₂ O ₅ · 24MoO ₃	3596.46
CaO	56.08	KIO ₃	214.00	PbCl ₂	278.10
Ca ₃ (PO ₄) ₂	310.18	KMnO ₄	158.04	Pb(NO ₃) ₂	331.20
CaSO ₄	136.14	K ₂ O	94.20	PbO ₂	239.19
CeO ₂	172.12	KOH	56.11	PbSO ₄	303.25
Cr ₂ O ₃	151.99	K ₂ PtCl ₆	486.01	SO ₂	64.06
CuO	79.54	KSCN	97.18	Sb ₂ O ₃	291.50
Cu ₂ O	143.08	K ₂ SO ₄	174.27	Sb ₂ S ₃	339.70
CuS	95.60	MgCO ₃	84.32	SiO ₂	60.08
CuSO ₄	159.60	Mg(C ₉ H ₆ ON) ₂ , Mg oxinate	312.62	SnO ₂	150.69
Fe(NH ₄)(SO ₄) ₂ · 12H ₂ O	482.19	MgCl ₂	95.22	SrCO ₃	147.63
Fe(NH ₄) ₂ (SO ₄) ₂ · 6H ₂ O	392.14	MgO	40.311	SrSO ₄	183.68
FeO	71.85	MgNH ₄ PO ₄	137.32	ThO ₂	264.04
Fe ₂ O ₃	159.69	Mg(NO ₃) ₂	148.32	TiO ₂	79.90
Fe ₃ O ₄	231.54	Mg ₂ P ₂ O ₇	222.57	U ₃ O ₈	842.09
FeS	87.91	MgSO ₄	120.37	V ₂ O ₅	181.88
FeS ₂	119.98	MnO ₂	86.94	WO ₃	231.85
HCHO ₂ , formic acid	46.026	Mn ₂ P ₂ O ₇	283.82	ZnO	81.37
HC ₂ H ₃ O ₂ , acetic acid	60.05			Zn ₂ P ₂ O ₇	304.68
H ₂ C ₂ O ₄ · 2H ₂ O, oxalic acid	126.07				

* Rounded to relative uncertainties between 0.02% and 0.002%.

WITHDRAWN



ELEMENTARY QUANTITATIVE ANALYSIS

Theory and Practice

Second Edition

W. J. Blaedel and V. W. Meloche
Professors of Chemistry at the University of Wisconsin



Harper & Row, Publishers
New York, Evanston, and London

Elementary Quantitative Analysis, Second Edition

Copyright © 1957, 1963

by Harper & Row, Publishers, Incorporated

Printed in the United States of America

All rights in this book are reserved.

*No part of the book may be used or reproduced
in any manner whatsoever without written permission
except in the case of brief quotations
embodied in critical articles and reviews.*

For information address

49 East 33rd Street, New York 16, New York.

Library of Congress catalog card number: 63-13613

PREFACE

This one-semester text should satisfy the requirements of a beginning course in inorganic quantitative analysis in the sophomore year. The topics of analytical chemistry are presented at two levels—in the text proper, and in the Supplement. The main body of the text is intended for study by both the chemistry major and the student majoring in other fields. Interesting proofs, details, and extensions of some topics in the main text are gathered into the Supplement, so that they will be available on an optional basis to those students and instructors who want them. This dual method of presentation will, we hope, lighten the teaching load of the instructor as well as the study load of the student.

Almost all the topics of elementary quantitative analysis are introduced in the text and the Supplement. Although prepared for the elementary course, the book contains more work than can be covered in the usual one-semester period. To facilitate the choice of study material by the student and the instructor, the text is organized in strict outline form.

Principles from other fields of science are involved in some subjects in quantitative analysis, such as statistics, equilibrium constants, electrode potentials, and instrumentation. We have attempted first to present these principles logically and independently, and then to apply them to quantitative analysis. Greater detail on topic sequence and organization is given in Chapter 1.

There is no arbitrary separation of theory, technique, and problem working, and an attempt has been made to stress all three equally. A rightful and necessary emphasis upon calculations is developed within the text, concurrently with the theoretical presentation of each topic. Insofar as is feasible, this is also done with experimental work.

The writing of a text is a humbling experience. In retrospect, we find that there are only a few ideas in this text which are our own. On each topic we have simply set down what seemed to us to be the best of the ideas of many people. Our methods and presentations have been greatly influenced by the concepts of other authors. It is impossible to express adequately our appreciation of the contributions of our colleagues,

graduate and undergraduate students, and secretaries, who gave so generously of their time, effort, and opinions. In particular, the help of Dr. Carter Olson in designing Experiment 22.1 is acknowledged.

Several important changes have been made in this second edition. Some modes of presentation have been altered or improved. Some topics of little general interest have been eliminated. Complexation and potentiometric titrations have been introduced. The problems after Chapter 3 have been very extensively revised.

This text should provide a core for the majority of work in the elementary analytical course. We know that our attempt to achieve depth in the Supplement has resulted in omission of a few topics that are considered important by some instructors. We hope that these omissions or inadequacies are few enough so that the usefulness of the text will not be impaired.

W. J. BLAEDEL
V. W. MELOCHE

Madison, Wisconsin

TABLE OF CONTENTS

Part One Introduction

1	The Study of Quantitative Analysis	1
2	The Quantitative Analytical Process	6
3	Mathematics Essential to Quantitative Analysis	15
4	Chemical Principles Fundamental to Quantitative Analysis	21
5	The Theory of Error and the Treatment of Quantitative Data	37

Part Two Gravimetric Analysis

6	Introduction to Laboratory Work	63
7	The Analytical Balance	70
8	Reagents and Gravimetric Techniques	96
9	Computations of Gravimetric Analysis	140
10	Analysis by Evolution, Determination of Water	150

11	Solubility and Solubility Product	160
12	The Formation of Pure Precipitates	177
13	Gravimetric Methods	210

Part Three Volumetric Analysis

14	The General Method of Volumetric Analysis	229
15	Volumetric Apparatus and Techniques	245
16	Titrations Based on Precipitation Reactions	273
17	Acid-Base Equilibria	316
18	Acid-Base Titrations	343
19	Redox Stoichiometry and Equilibria	395
20	Redox Titrations	438

Part Four Special Topics

21	Spectrophotometry	505
22	Instrumental Methods of Chemical Analysis	537
23	Complexation Titrations	559
24	The Literature of Analytical Chemistry	600

Supplement

3	Mathematics Essential to Quantitative Analysis	610
5	The Theory of Error and the Treatment of Quantitative Data	613
7	The Analytical Balance	649
9	Computations of Gravimetric Analysis	670
10	Analysis by Evolution. Determination of Water	676
11	Solubility and Solubility Product	701
12	The Formation of Pure Precipitates	716
13	Gravimetric Methods	733
14	The General Method of Volumetric Analysis	745
15	Volumetric Apparatus and Techniques	746
16	Titration Based on Precipitation Reactions	754
17	Acid-Base Equilibria	768
18	Acid-Base Titrations	778
19	Redox Stoichiometry and Equilibria	807
20	Redox Titrations	818
21	Spectrophotometry	867
22	Instrumental Methods of Chemical Analysis	895

Appendices

IA	Table of Four-Place Logarithms	901
IB	Table of Five-Place Logarithms (10000–20000)	906
IIA	Table of Ordinates of the Normal Curve	908
IIB	Table of Areas under the Normal Curve	909
III	Individual Locker Equipment for Experiments in This Book	910
IVA	Chemical Reagents	911
IVB	Solutions of Acids, Bases, and Salts	913
IVC	Indicator Solutions	914
IVD	Miscellaneous Solutions	915
V	Solubility Products	916
VI	Hydrated Ion Diameters and Activity Coefficients (25°C)	921
VIIA	Ionization Constants of Inorganic Acids and Bases (25°C)	923
VIIB	Ionization Constants of Organic Acids and Bases (25°C)	925
VIII	Acid-Base Indicators	928
IX	Standard Redox Potentials in Aqueous Solution (25°C)	930
X	Selected Stability Constants	932

List of References	933
---------------------------	------------

Index	943
--------------	------------

End Papers

Table of Atomic Weights, 1961	}	<i>inside front cover</i>
Formula Weights of Common Radicals		
Formula Weights of Common Substances		
Periodic Table of the Elements		<i>inside back cover</i>

LIST OF EXPERIMENTS

7.1	Operation of the Balance	87
7.2	Determination of the Zero Rest Point	88
7.3	Determination of Sensitivity	88
7.4	Checking the Weight Set (10-mg Rider Balance)	89
7.5	Checking the Weight Set (Chain Balance)	90
7.6	Determination of the Balance-Arm Ratio	91
7.7	Determination of an Unknown Weight Difference	91
10.1	Indirect Determination of Water	156
13.1	Gravimetric Determination of Chloride as AgCl	214
13.2	Gravimetric Determination of Sulfate as BaSO ₄	221
15.1	Calibration of the 50-ml Pipet	266
15.2	Calibration of the Volumetric Flask	267
15.3	Calibration of the 50-ml Buret	268
15.4	Relative Calibration of the 250-ml Flask and the 50-ml Pipet	269
16.1	Preparation of Standard AgNO ₃ and KSCN Solutions	291
16.2	The Fajans Titration of Chloride	295
16.3	The Volhard Determination of Silver in an Alloy	298
16.4	The Volhard Determination of Chloride	301
16.5	The Mohr Determination of Chloride	303
18.1	Preparation of Standard HCl and NaOH Solutions	365
18.2	Determination of Na ₂ CO ₃	370
18.3	Determination of KHP	371
18.4	Titration of H ₃ PO ₄ with a pH Meter	371
18.5	Titration of an HCl-H ₃ PO ₄ Mixture	376
18.6	Kjeldahl Determination of N as NH ₃	378
20.1	Determination of Iron in an Ore	476
20.2	Determination of Calcium in Limestone	481
20.3	Determination of Copper in an Ore	488
21.1	Spectrophotometric Determination of Manganese in Steel	526
22.1	Potentiometric Determination of Chloride	550
23.1	Determination of Ca, Mg, and Fe in Limestone by EDTA Titration	590

1 THE STUDY OF QUANTITATIVE ANALYSIS

1A. PRIMARY OBJECTIVES

The study of analytical chemistry provides ideal training for nearly all scientists. A course in quantitative analysis equips the student with the ability to plan and to execute experimental work; it develops in him the ability to record and to interpret such work; and it trains him to understand and to communicate what he has done. These scientific abilities are extremely important; it is through them that the individual worker applies his knowledge and contributes to mankind's progress.

Furthermore, a course in quantitative analysis should impress upon the student the wide importance and the applicability of analytical chemistry and its relation to other branches of science.

Finally, and obviously, the course should extend the student's chemical knowledge and technique beyond the introductory level of general chemistry.

1A.1. Scientific Ability and Quantitative Analysis

Scientific ability is not a single characteristic, nor is it acquired without effort. It is a composite of many characteristics, acquired through many years of training, work, and concentration. It is more than the ability to assimilate theory, or to reason abstractly, or to plan well, or to use one's hands, or to convey ideas; it is the coordinated application of all these skills to the acquisition and extension of knowledge. The course in quantitative analysis is a very important link in the chain of

studies that develops this scientific ability in the chemist. With its multiple emphasis on theory, laboratory work, and high accuracy in the analysis of unknown samples, quantitative analysis is one of the most valuable courses in the student's training. No other chemistry course may be satisfactorily substituted for it.

1A.2. Importance of Quantitative Analysis

Quantitative analysis derives much of its knowledge from the other three divisions of chemistry. For example, knowledge of the properties of substances on which analyses are based is drawn from inorganic and organic chemistry. The methods and instruments used for measurement in analyses are drawn from physics and physical chemistry.

But, conversely, almost any study in chemistry has its analytical aspect, whether it is in research, development, or production. Analytical chemistry permeates the other fields of chemistry to such an extent that no chemist may consider himself free of its influences. With few exceptions, quantitative analysis is essential to all other areas of chemical science.

In spite of the importance of analytical chemistry to almost every chemical problem, workers often attempt to minimize or circumvent the analytical phase, for a reason that is understandable. Since the analytical effort is usually only a means to an end, there is often impatience with such a means, particularly if it is exacting or time consuming.

It is not the purpose of this text to extol the virtues of analytical chemistry. It is the purpose, however, to develop an awareness of the importance of analytical chemistry to all chemical problems, and to emphasize the fact that neglect of the analytical phase usually causes more confusion and loss of effort than is apparently saved by such negligence. The chemist who moves heaven and earth to avoid what he considers a mundane gravimetric analysis is not a good chemist. Also, the chemical engineer who takes a process into a pilot or semiworks stage without first making thorough provision for proper sampling and analysis at all steps materially increases the chances of confusion and failure of the process.

As far as practical importance is concerned, hundreds of millions of quantitative determinations are performed yearly in monitoring the processes and materials of American metallurgical industries alone. Comparable effort is expended in other chemical industries. Every individual who reads this text has probably undergone clinical tests and determinations; without the hundreds of millions of these that are performed yearly, our physicians and hospitals could not function properly. It is no exaggeration to say that without chemical analysis,

our industries and the civilization that they support could not exist as we know them today.

1B. ORGANIZATION OF THE TEXT

1B.1. Topic Sequence

There are four parts to this one-semester text: Part One, Introduction; Part Two, Gravimetric Analysis; Part Three, Volumetric Analysis; and Part Four, Special Topics. The theory, practice, and problem working of elementary quantitative analysis are integrated throughout, on the conviction that confusion arises in any attempt to separate or deemphasize one of them with respect to the other two.

The first five chapters include the prerequisite and introductory topics of quantitative analysis. This first chapter considers the study of quantitative analysis. The quantitative analytical process is outlined in an introductory way in Chapter 2. Chapters 3 and 4 summarize and review some essential aspects of elementary mathematics and chemistry. The fifth chapter introduces the concepts of accuracy, precision, computation, and the treatment of quantitative data.

In practice, laboratory work should begin immediately. It is therefore recommended that systematic study of the text begin with Chapter 6, and that the introductory chapters (1-5) be studied concurrently or intermittently, as the need arises. These two groups of chapters (1-5 and 6-13) are written with this necessity in mind. But the sooner the student masters the content of chapters 1 to 5, the more thoroughly will he understand the work of the rest of the course.

Chapter 6 introduces the student to laboratory work. Chapters 7 and 8 cover the analytical balance and gravimetric techniques. Chapters 9 and 10 deal with gravimetric calculations and analysis by evolution, which represents the simplest kind of gravimetric procedure. After these chapters the theory of gravimetric precipitation processes is presented, including solubility product (chapters 11, 12). A detailed description of two methods (for chloride and sulfate) and a summary of some others close the section on gravimetric analysis (Chapter 13).

After this, the transition to volumetric analysis by precipitation processes is easy (chapters 14-16). Acidimetry and alkalimetry (chapters 17, 18) follow, together with the quantitative treatment of acid-base equilibria, which are more complicated than those involving only solubility product. Redox titration, including study of the table of standard potentials, may be made the last topic of the elementary course (chapters 19, 20).

Part Four presents some topics that may be of interest to certain

groups of students and instructors. They include spectrophotometry (Chapter 21), instrumental methods of analysis (Chapter 22), complexation titrations (Chapter 23), and the literature of analytical chemistry (Chapter 24).

This sequence provides the opportunity to keep the lecture and laboratory work nearly abreast of each other and to distribute the introduction of new concepts evenly over the whole semester, as they increase in complexity.

1B.2. Use of the Supplement

The difference between teaching quantitative analysis to a chemistry major and to a student majoring in another field does not lie in the number or the kinds of topics studied, but only in the fact that the chemistry major studies some topics in greater detail. It is expected that this text will prove suitable for both kinds of students. By organization of the material according to the outline form, each topic is sharply delineated to facilitate study, reference, assignment, and review. The chemistry major or the advanced student who wishes to pursue any subject further than its elementary phase should make use of the Supplement. This is not itself readable with continuity, but is rather a series of notes that prove, amplify, or extend some of the topics of the text. The Supplement should aid the student to bridge the gap between the elementary phases of a subject and the advanced phases found in the voluminous and often bewildering array of chemical literature.

There are many illustrative examples throughout the text and Supplement. At the ends of the chapters discussion questions and problems are arranged according to sections. Problems in the Supplement are more challenging than those in the text. Answers are not given to the discussion questions, but are provided to about half of the problems, so that the student may have some check on his work as he proceeds.

1B.3. Experimental Work

As far as possible, the laboratory work is organized in such a way that the student will have some assurance of the correctness of his technique and equipment before he invests time in the analysis of unknown samples. For example, balance techniques and weights are checked before gravimetric analyses are undertaken. Volumetric equipment is calibrated, not so much to check the equipment as to check the student's technique in using it. Standard solutions are standardized by more than one method wherever this is possible. Failure to perform such checks faithfully is practically a guarantee of poor results on unknown

samples; furthermore, the time apparently saved by omission of such checks is generally lost several times over in attempts to rectify errors that could have been avoided by properly performing the checks. As many factors as possible should be checked before an analysis, rather than after.

Most of the usual determinations of elementary quantitative analysis are described in considerable detail, so that the student may work as independently as possible. They should be suitable for the greater part of the usual laboratory work, and not many special directions should have to be added for any particular instructor's purpose.

1C. THE STUDY OF QUANTITATIVE ANALYSIS

Both theoretical and experimental knowledge are fundamental to any science. Although separated for ease in teaching and study, these two kinds of knowledge are intimately related, and must constantly be correlated by the student during the learning process. In the laboratory it should be the student's constant effort to relate his actions to his theoretical knowledge. In the classroom, or when the text is being read, the process should be reversed, and the student should attempt to picture or interpret theoretical concepts in terms of concrete laboratory situations. If this is not done, the student's understanding of the subject will remain incomplete.

2 THE QUANTITATIVE ANALYTICAL PROCESS

2A. THE BRANCHES OF ANALYTICAL CHEMISTRY

Broadly speaking, *analytical chemistry* refers to all techniques and methods for discovering the identity and/or the amounts of the constituents in a sample. *Qualitative analysis* is concerned with the nature and the kinds of materials in the sample, without specific interest in the exact amounts present. *Quantitative analysis* is concerned with the amounts of various materials in the sample, and the results of such analysis are expressible only in terms of numbers. In general, the qualitative composition of a sample must be known before a quantitative analysis may be made; there is no point in trying to determine the amount of a constituent unless it is first known whether or not that constituent is present at all. Also, it must be known if interfering substances are present.

Quantitative analysis itself may be further divided into two branches. *Inorganic analysis* deals with the elements and their various inorganic compounds. This book is restricted almost entirely to inorganic analysis. *Organic analysis* deals with carbon compounds containing hydrogen, oxygen, and a small number of other elements. Procedures and techniques are considerably different from those of inorganic analysis, and are usually made the subject of a more advanced course of instruction.

In inorganic quantitative analysis some elements are encountered with much greater frequency than others. The methods of this text are restricted almost entirely to this class of common elements. The student who has had one semester of quantitative analysis should be conversant

with at least one method for the determination of each of the following: Ag, Al, As, Br, C, Ca, Ce, Cl, Cr, Cu, F, Fe, H, Hg, I, K, Mg, Mn, Mo, N, Na, Ni, O, P, Pb, S, Sb, Si, Sn, Ti, V, W, Zn. The remaining elements are met only occasionally, in connection with special problems.

2B. OUTLINE OF THE QUANTITATIVE ANALYTICAL PROCESS

The quantitative analytical process may be divided into five stages: (1) preliminary consideration, (2) sample preparation, (3) isolation of the sought-for constituent in measurable form, (4) measurement of the sought-for constituent, and (5) calculation and presentation of results. In the following sections each of these phases is discussed in an introductory way.

The above outline does not represent a universal process through which all samples must go in order to be analyzed; in many cases it is possible to omit or to combine some steps of the process, with a consequent saving in labor. The actual sequence of the steps will also depend on the individual analysis at hand. However, even though there are wide departures in specific cases from the above procedure, it is quite representative of many analytical methods.

It should be mentioned that the elementary course in quantitative analysis concentrates on steps 4 and 5 (measurement and calculation). Study of the first three stages cannot be undertaken, except in a most elementary way, until familiarity with the methods of measurement is gained.

2B.1. Preliminary Consideration

There are several aspects of an analysis that must be clarified even before a sample is taken, and that help to determine how the subsequent stages of the analysis may best be carried out.

First of all, it is necessary to decide on the nature of the analysis desired. Is a *complete* analysis of the whole sample necessary, or is a *partial* analysis for just one or a few constituents satisfactory? Is an *ultimate* analysis for each of the elements in the sample required, or is a *proximate* analysis for certain groups of elements adequate? For example, in limestone analysis, must Fe_2O_3 , Al_2O_3 , etc., be determined as separate components, or may their sum be reported as R_2O_3 ?

The amount of material available for analysis has an important bearing on the techniques that must be used. Chemical methods are sometimes classified according to the size of the sample used for analysis, as shown in Table 2.1. Techniques may vary tremendously from one class to another. Where samples from 0.1 to 1 g are available, the ordinary *macromethods* described in this text are acceptable. Usually, special

and increasingly painstaking practice is required as the sample size decreases. Differentiation among the classes of methods is not sharp, and the procedures of any one class may be extended in some cases to considerably larger or smaller sample sizes than the ones given in Table 2.1 (K7).** Many ultra- and submicrogram methods are quite new—still in the developmental or research stage.

TABLE 2.1

CLASSIFICATION OF ANALYTICAL METHODS ACCORDING TO SAMPLE SIZE*

Name of Class	Approximate Sample Size Taken for Analysis
Ordinary, or macromethods . . .	100 mg
Semi-micromethods	10 mg
Micromethods	1 mg
Ultramicromethods	0.001 mg, or 1 μ g
Submicrogram methods	0.01 μ g

*Reprinted from P. L. Kirk, *Quantitative Ultramicroanalysis* (New York: Wiley, 1950), Table 1, by permission of the publisher.

The technique of analysis depends upon whether the sought-for constituent is a *major*, *minor*, or *micro constituent*, i.e., comprises more than 1%, 0.01–1%, or less than 0.01% of the sample weight. Sandell (S2) gives an excellent introduction to the procedures and objectives of trace analysis.

The choice of an analytical method is often determined by the accuracy desired and by the purpose for which the analysis is made.

The history of the specimen or sample usually indicates the constituents that may be present. If they are not known, a qualitative analysis is necessary. The history may even reveal roughly how much of certain constituents is present, as well as other useful information such as sampling validity and good solvents.

2B.2. Sample Preparation

The primary purpose of the *sampling procedure* is to obtain a workable sample of laboratory size that properly represents the average composition of the bulk specimen from which the sample is taken.

Of all the operations involved in the analytical process, sampling is probably done incorrectly more often than any other operation. An incorrectly taken sample may invalidate a good analysis and give a completely erroneous idea of the specimen from which it is taken. The classic example of incorrect sampling procedure and its ridiculous consequences is given by the fable of the blind men and the elephant. The consequences are sometimes no less ridiculous for incorrect chemical

**See page 933 for the List of References.

sampling. Samples given to students in the elementary course may be considered homogeneous and properly taken.

Sample preparation also includes measurement of the amount taken for analysis. Solid samples are usually weighed out with a balance. Gaseous or liquid samples are generally measured out most easily and rapidly by volume. The precision in measuring out the sample should be at least as great as the precision desired in the analysis. Most solid samples contain appreciable amounts of moisture, and are dried under conventionally selected conditions before being weighed. Results are then reported on a dry basis.

2B.3. Isolation of the Sought-for Constituent

After the sample is measured out, the sought-for constituent is seldom in a condition suitable for measurement. Most methods of determination require dissolution of the sample as a first step—occasionally the most troublesome part of the whole analytical process. Sometimes the wanted substance cannot be dissolved by any solvent, and a high-temperature fusion is required to convert it to a soluble form.

After solution, any interfering substances must be removed before the sought-for constituent is measured. The actual processes used for the separation of interferences vary widely. The effort required to separate the interferences depends greatly on their similarity to the desired substance, and also upon their relative amounts. Occasionally, interferences may be converted to chemically different and noninterfering forms, without having to be removed. Sometimes the interferences are removed from the solution by precipitation, volatilization, solvent extraction, ion exchange, or electrodeposition, leaving the sought-for constituent. Sometimes the desired substance itself is removed from the solution and recovered, leaving the interferences.

The separation is not always carried out as a distinct step following the solution of the sample. As a matter of fact, each operation from beginning to end of the analytical process is usually carried out in such a way as to afford the maximum separation. For instance, it may be possible to “pick over” the original sample to remove interferences. Sometimes a solvent may be chosen that leaches out the desired substance and leaves most of the unwanted compounds behind. For example, Fe may be leached from an ore with hydrochloric acid, leaving silica undissolved.

It might seem that the comprehensive and systematic schemes that have been worked out for qualitative analysis should be applicable to separations for quantitative analysis. Such systems have been devised (§35). However, complete separation from all substances is seldom nec-

essary, since the number of interferences for most quantitative methods is quite low. Generally, therefore, any quantitative analytical method is rather restricted in application, depending not only upon the particular substances present, but upon their amounts also. For example, the procedure for the determination of traces of Cu in plant tissue is highly different from the determination of Cu in its ores. It happens frequently that a regular procedure for the determination of a desired substance is inapplicable, simply because the sample contains a substance not provided for in the scheme, or because the sought-for substance is present in amounts different from those provided for. It is for such reasons that the preliminary considerations are extremely important.

Even after interferences have been separated, the desired constituent may still not be in a form that is suitable for measurement. Conversion to a measurable form constitutes the last part of the isolation stage. Such a form may be a precipitate, if the method of measurement involves weighing; or, if a titration is carried out, the measurable form may be a particular ionic state of the sought-for constituent that reacts quantitatively with a standard solution. In some methods of analysis the separation and conversion occur in a single step, as in the gravimetric determination of sulfate in a mixture of NaCl and Na₂SO₄ by precipitation as BaSO₄.

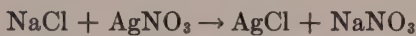
2B.4. Measurement of the Sought-for Constituent

It is this stage of the analytical process that is studied most intensively during the elementary course, and is often popularly and incorrectly thought of as "quantitative analysis." It is in this stage that an *analytical technician*, with little more than some skill and the ability to follow directions, may perform a good "analysis" after some practice. But the analytical technician performs only a part of the analytical process. To go satisfactorily through the whole process requires an *analytical chemist*, a person with the basic understanding and ability to select his procedure and modify each stage so that the objectives of the analysis are achieved.

Methods of measurement are of two general kinds: classical and physico-chemical. In the *classical* or *stoichiometrical methods*, the sought-for substance is decomposed, or is made to react with another substance, according to a well-defined chemical equation. By measuring the amount of product formed, or of reagent used, the amount of sought-for substance may be calculated from the laws of definite and combining proportions. Classical methods are of three kinds: gravimetric, volumetric, and gasometric.

In the *gravimetric method* the desired substance is made to react quantitatively with an excess of another substance. A product of the reaction is then weighed. From the amount of product, and the equation for the reaction, the amount of sought-for substance may be calculated.

Many gravimetric methods involve conversion of the sought-for substance to an insoluble precipitate, which is easily isolated and weighed. For example, to find the NaCl content of a mixture of NaCl and Na₂SO₄, it would be too difficult to extract and weigh the NaCl as such from this mixture, since both salts are soluble. Instead, the sample is dissolved and an excess of AgNO₃ is added, which converts the NaCl to insoluble AgCl.



The AgCl is filtered off and weighed. Since the AgNO₃ is in excess, the yield of AgCl is determined by the amount of NaCl in the sample. The amount of NaCl may therefore be calculated from the weight of AgCl produced, thus.

$$g \text{ NaCl} = g \text{ AgCl produced} \times \frac{\text{MW NaCl}}{\text{MW AgCl}}$$

Other gravimetric methods involve decomposition, the weight of a product or residue being determined. The Cu content of a sample containing CuSO₄ and Na₂SO₄ may be found by putting the sample into solution, electroplating the Cu onto an inert electrode, and weighing. Water of hydration in a sample may be determined by heating to drive off the water. The water vapor may be carried off in a dry gas stream and collected in a previously weighed absorption tube, or the residue may be weighed and the water content calculated by difference.

In the *volumetric method* the wanted substance is made to react quantitatively with a reagent substance, added as a standard solution whose concentration is known. When reaction is complete, the amount of sought-for substance may be calculated from the measured volume of standard reagent used; this is different from the gravimetric method, where the amount of sought-for substance is calculated from the weight of a product. The technique of finding how much standard reagent is required to react exactly with the desired substance is called a "titration." Some signal or indicator is needed to show when an equivalent amount of reagent has been added, and when none of the sought-for substance remains.

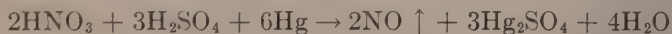
The NaCl content of the previously mentioned NaCl-Na₂SO₄ mixture may be determined by a volumetric method, based upon the same reaction that was used for the gravimetric determination. The sample is dissolved, an indicator is added, and the solution is then titrated with

a standard AgNO_3 solution of known concentration. The volume of AgNO_3 required to change the indicator is observed. From this volume and the concentration of AgNO_3 , the weight of NaCl in the sample may be calculated.

Volumetric methods may be based upon any kind of chemical reaction that goes quantitatively, such as precipitation, neutralization, complexation, and oxidation-reduction.

In the *gasometric method* the sought-for substance is made to react or decompose completely, the volume being measured for a gaseous product produced, or for a gaseous reagent consumed. After corrections for temperature and pressure are made, the amount of sought-for substance is calculated from this measured volume.

Nitrates may be determined by measuring the volume of NO produced in a closed system on reduction with Hg .



Often the desired substance may be a component of a gaseous mixture. In a mixture containing other gases, such as nitrogen and oxygen, CO_2 may be determined by passing the mixture through an absorbent selective for CO_2 , such as soda-lime. The difference in volumes before and after absorption represents the volume of CO_2 in the sample.

In the *physico-chemical* or *nonstoichiometrical methods*, some measurable physical property is taken as a measure of the amount or concentration of the sought-for substance. Among such properties are density, melting point, conductivity, color, refractive index, optical rotation, etc. Such procedures often have the advantages of speed, simplicity, objectivity, and precision. Also, some of these properties may be precisely measurable at trace concentrations of the wanted substance, where ordinary gravimetric and volumetric methods may fail completely. Finally, some physical methods do not destroy or even alter the sample, as chemical methods always do.

Measurement of a single physical property often serves as a simple procedure for analyzing two-component mixtures. Thus to analyze a benzene-carbon tetrachloride mixture, a property such as specific gravity is measured. Reference to a graph of specific gravity plotted against composition immediately gives the composition of the mixture.

The color of solutions of colored substances, like ammoniacal cupric ion or KMnO_4 , may be measured objectively at rather low concentrations, and taken as a measure of the concentration of the colored substance. Most metal ions form highly colored complex substances with the proper reagents (mostly organic), and may be determined with reasonable accuracy in trace amounts far below the amounts required for ordinary gravimetric or volumetric methods.

For reasons mentioned in Chapter 22, physico-chemical methods cannot be stressed in the elementary course, which is concerned chiefly with classical methods.

In closing this survey of methods of measurement, *selectivity* should be defined. A method of determining a substance is said to be highly selective for that substance if the measured quantity depends only upon the amount of that substance, and is not affected by other substances that may be present. In other words, a highly selective method is one for which there are very few interferences. High selectivity is a desirable characteristic, since it greatly reduces the need for prior separations.

Most of the highly selective procedures involve physico-chemical methods of measurement. Some spectrographic analyses for certain elements may be performed without any prior separation at all; many elements that would interfere severely with other methods of determination do not have to be removed. Many colorimetric procedures are also quite selective.

On the other hand, some methods of measurement are completely nonselective. For these everything except the desired substance must be removed before measurement. Measurement by weight is nonselective. In the determination of sulfate as BaSO_4 , for example, the weighable product must be pure BaSO_4 . Any other weighable material causes error.

TABLE 2.2
SURVEY OF ANALYTICAL PUBLICATIONS
ON VARIOUS METHODS OF MEASUREMENT

TYPE OF METHOD DESCRIBED IN THE PUBLICATION	PER CENT OF TOTAL PUBLICATIONS		
	Year 1929-30 (M15)	Year 1950-51 (M15)	Year 1955 (F3)
Titrimetric.....	30.8	27.0	22.0
Gravimetric.....	18.7	7.3	6.5
Spectrophotometric.....	11.1	24.4	37.7
Other, mostly instrumental..	39.4	41.3	33.7

Table 2.2 is a survey of analytical publications, according to the method of measurement that was used. It is clear that over the past three decades there has been a shift in emphasis from gravimetric to colorimetric and spectrophotometric procedures. On the other hand, titrimetric methods continue to be of prime importance.

2B.5. Calculation of Results

A quantitative analytical result is not very useful unless its precision is indicated. Care must be used not to express the result in a way that implies far more precision than was used in obtaining the result. Also, in computing the result, precision must not be lost that may have required expenditure of considerable experimental effort. The conventions and procedures used in computing and expressing quantitative data are discussed in greater detail in Chapter 5.

3 MATHEMATICS ESSENTIAL TO QUANTITATIVE ANALYSIS

3A. PREREQUISITE MATHEMATICS

It is supposed that the student has had mathematics through one semester of college algebra. Those topics of elementary mathematics that are necessary or particularly useful for quantitative analysis are listed below, but are not reviewed because they may be found easily in elementary texts. Instead, problems are given on each topic at the end of this chapter. If working the problems on any particular topic proves difficult, this topic should be reviewed with the aid of a good text. Deficiency in mathematics inevitably leads to difficulty in quantitative analysis; it is not possible to concentrate upon chemical principles while stumbling over mathematical details.

Notation and definitions. The meaning of the following terms should be clear: operational signs, factors, powers, and roots.

Simple linear algebraic equations. The student should be familiar with the four steps in setting up and solving a linear equation: (1) translation of the conditions of the problem (usually stated in common language) into algebraic language; (2) formulation of the equation; (3) solution; and (4) check.

Exponents. The student should be able to handle exponents in the common operations of addition, subtraction, multiplication, division, taking roots, and raising to a power.

Logarithms. The student should be able to use the log tables (Appendix I) to perform the operations of multiplication, division, taking roots, and raising to a power.

Slide rule. Ability to use a slide rule is necessary. As a minimum, the use of the *A*, *B*, *C*, *D*, *K*, and *Log* scales in multiplication, division, squaring, cubing, rooting, and finding logs should be understood. An inexpensive rule is adequate. Only a few hours are required to learn these operations, and these hours are saved many times over in the analytical course alone.

3B. QUADRATICS AND EQUATIONS OF HIGHER DEGREE

Not all equations are linear. *Quadratic equations* may contain terms involving x^2 , even when reduced to the simplest form. *Equations of higher degree* may contain terms involving higher powers of x , such as x^3 and x^4 . The solution of such equations requires considerably more effort than simple equations of the first degree.

Although there are formulae for the rigorous solution of quadratic equations, and even cubic and quartic equations, the practical application of these formulae is often troublesome. For equations of higher degree, and equations containing exponential or trigonometric functions of x , there are no rigorous methods of solution, and *approximate methods* must be used.

For equations arising from physical or chemical problems, methods of approximation do not involve nearly the trouble that the uninitiated believe. There are several systematic procedures for making successive approximations that converge upon a satisfactory answer in very few steps. Also, for these chemical or physical problems the estimates are often aided by a rough prior knowledge of what the answers should be.

A few simple procedures for solving nonlinear equations are given below and in the Supplement (pp. 610–12). There are more systematic and elegant procedures, some of which arrive at suitable answers in a very few estimates, but these methods are not so simple or so easily understood as the methods below (C12).

3B.1. The Quadratic Formula

Every quadratic equation may be put into this form:

$$ax^2 + bx + c = 0 \quad (3.1)$$

Solving, we obtain

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a} \quad (3.2)$$

Example. Calculate the solubility, x , of a substance from the following equation, which is of the type sometimes obtained in problems involving the solubility product: $x^2 + 0.010x - 0.0040 = 0$.

$$x = \frac{-0.010 \pm \sqrt{(0.01)^2 + 0.0160}}{2} = 0.058$$

Check:

$$(0.058)^2 + (0.010)(0.058) - 0.0040 \stackrel{?}{=} 0$$

$$0.0039 - 0.0040 \cong 0$$

The negative root cannot have meaning, since no substance can have a negative solubility.

3B.2. Method of Neglecting Small Quantities

Very often problems involving solubility products or equilibrium constants result in such equations as

$$x^2(x + a) = K$$

This is a cubic equation, not subject to simple rigorous solution. There are two cases where simplification becomes possible.

Case I. $a \gg x$. Then the equation becomes a simple quadratic, since x may be neglected compared to a .

$$x^2(x + a) = K$$

$$x = \sqrt{K/a}$$

Case II. $a \ll x$. Then the equation becomes a simple cubic, since a may be neglected compared to x .

$$(x^2)(x + a) = K$$

$$x = \sqrt[3]{K}$$

This is all well and good, but how is the student to know, with nothing but the original equation before him, whether x is much greater or less than a ? The answer is that the student may assume that one case holds, and may solve the equation for a numerical value of x . He may then test this answer. If comparison of the numerical value of x with a shows the answer to be *consistent* with the assumption, the answer is valid. On the other hand, if the answer is *inconsistent*, the student may assume the other case, may solve for x , and may then test the (different) answer obtained. If the second value of x is consistent with the second assumption, the second answer is valid. If the second answer is also *inconsistent*, the method of neglecting small quantities is inapplicable.

Since the resulting equations are very simple, the solutions can be worked out quickly. Usually the circumstances of the problem allow insight to the better assumption.

Example. The hydrogen-ion molarity (x) in a solution containing 0.010 M acetic acid and 0.010 M sodium acetate may be calculated from the following equation: $x(0.010 + x) \div (0.010 - x) = 1.8 \times 10^{-5}$. Solve this equation for x .

Acetic acid is a weak acid, and the sodium acetate serves to repress its ionization even more, so that it is quite likely that $x \ll 0.010$. If this is the case, the x terms may be neglected compared to 0.010.

$$\frac{x(0.010 + \cancel{x})}{(0.010 - \cancel{x})} = 1.8 \times 10^{-5} \quad \text{or} \quad x = 1.8 \times 10^{-5}$$

Test answer: 1.8×10^{-5} is much less than 0.010. Hence the answer is consistent with the assumption, and acceptable.

If the other possibility had been assumed, namely, that $0.010 \ll x$, the terms 0.010 would have been dropped in comparison with the x terms.

$$\frac{x(\cancel{0.010} + x)}{(\cancel{0.010} - x)} = 1.8 \times 10^{-5} \quad \text{or} \quad x = -1.8 \times 10^{-5}$$

Test answer: Since 0.010 is not much less than -1.8×10^{-5} , the answer is not consistent with the assumption. Furthermore, a negative concentration is meaningless. Hence the answer is invalid.

Although the original equation is solvable with the quadratic formula, the method of approximation is faster, simpler, and preferable.

PROBLEMS

Section 3A

1. For practice in algebraic operations, find the numerical values of the following expressions, where $a = 1$, $b = 2$, $c = 3$, $d = 4$, $x = 5$, $y = 6$, $z = 0$.

- | | | | |
|--------------------|------------------|-------------------------------------|---------------------|
| (a) $20x$ | <i>Ans.</i> 100. | (l) $(b^2)^d$ | |
| (b) abc | | (m) $ay + 2c + (3d + 8)2$ | <i>Ans.</i> 52. |
| (c) ab^3 | <i>Ans.</i> 8. | (n) $bx^2 + y + b(\sqrt{db^2} + 4)$ | |
| (d) $abcz$ | | (o) $(\sqrt[5]{dy + c})^2$ | <i>Ans.</i> 243. |
| (e) $2b^cx$ | <i>Ans.</i> 80. | (p) $c[b^2 + (b + y)^2 + 7]$ | |
| (f) 10^e | | (q) $\sqrt{[b + c^2(2 + x)]d - d}$ | <i>Ans.</i> 16. |
| (g) $ab^2/2dx$ | <i>Ans.</i> 0.1. | (r) $[b(b + x) - c][dx - 2y] + xy$ | |
| (h) \sqrt{dx} | | (s) $(a/b)[(c + d)/(x + y)]^{d/b}$ | |
| (i) $(d^2)^{1/4}$ | <i>Ans.</i> 2. | | <i>Ans.</i> 49/242. |
| (j) $\sqrt[3]{db}$ | | (t) $(a + b + c + d^2)^{b-2a}$ | |
| (k) $c\sqrt{dx^3}$ | <i>Ans.</i> 30. | | |

2. Of the following problems, a through l are exercises in translation of common language into algebraic language; m through s involve simple linear algebraic equations.

(a) If a man builds x toys in one hour, how many will he build in 10 hours? In z hours? *Ans.* 10 x ; xz .

(b) If a man walks x miles per hour, how long will it take him to walk 20 miles?
 p miles? $\sqrt[3]{n}$ miles?

(c) If one part of 69 is m , what is the other part? *Ans.* $69 - m$.

(d) By how much does 18 exceed $9x$?

(e) If the sum of two numbers is 11, and one is x , what is the other?

Ans. $11 - x$.

(f) Express x yards plus b feet as inches.

(g) A man has x dollars. If he spends b half dollars and c nickels, how many cents has he left? *Ans.* $100x - 50b - 5c$ cents.

(h) Three sides of a rectangular box measure z , b , and c inches, respectively. What is the volume?

(i) If the sum of a plus b dollars is equally divided between two people, what is the share of each? *Ans.* $\$(a + b)/2$.

(j) A vehicle starting from rest gains velocity at the rate of b feet per second per second. What is the velocity at the end of 2 seconds? x seconds?

(k) A rectangular floor is x feet long and z feet wide. In the center is placed a carpet, a feet square. How many square feet of floor are bare?

Ans. $xz - a^2$ square feet.

(l) A chemist starts with b grams of substance. He purifies this and obtains an 80% yield. There is a further loss of 10 g in packaging. How much substance is in the package?

(m) The sum of two numbers is 150, and the greater is four times the smaller. What is each number? *Ans.* 30, 120.

(n) Divide 37 into two parts, so that one part shall be greater by 5 than the other.

(o) Find five consecutive numbers whose sum is 60. *Ans.* 10, ..., 14.

(p) Divide 27 into two parts so that twice the smaller part exceeds the greater by 3.

(q) Two men start from the same place and travel in opposite directions, one at 20 miles per day, and the other at 50 miles per day. In how many days will they be 770 miles apart? *Ans.* 11 days.

(r) Two carboys contain equal volumes of acid. From one carboy, 22 l are withdrawn, and from the other, 10 l. The quantity now remaining in one carboy is three times that in the other. What was the original volume in each carboy?

(s) A quantity of money is divided among A , B , and C in such a way that A receives \$6 more than B , and \$8 more than C . If A receives twice as much as B , how much does each receive, and what is the original sum? *Ans.* \$12, \$6, \$4, \$22.

3. For practice in handling exponents, find numerical answers to the following:

- | | | | |
|--|--------------------------------------|---|-------------------------------------|
| (a) $(1.02 \times 10^{-5})^3$ | <i>Ans.</i> 1.04×10^{-10} . | (f) $7^3 + 2^3$ | |
| (b) $(2.0 \times 10^{-4})^{1/2}$ | | (g) $(4.0 \times 10^{-5})^{3/2}$ | <i>Ans.</i> 2.53×10^{-7} . |
| (c) $(5.0 \times 10^{27})^{-2}$ | <i>Ans.</i> 4.0×10^{-56} . | (h) $[2.0 \times 10^{-13} + 2.0 \times 10^{-14}]$ | |
| (d) $[(2.0 \times 10^{-6}) \div (8.0 \times 10^{-8})]^{1/2}$ | | $- 1.1 \times 10^{-13}]^{1/2}$ | |
| $\times 10^{-14}$ | | (i) $(1.6 \times 10^{-5})^{1/3}$ | <i>Ans.</i> 4.0×10^{-3} . |
| (e) $10^{-5} + 10^{-3}$ | <i>Ans.</i> 0.00101. | (j) $(1.5 \times 10^{-5})^{1/3}$ | |

4. Work out the following expressions, using logarithms.

- | | | | |
|--|--------------------|---|--|
| (a) (1.234×2.765) | <i>Ans.</i> 3.412. | (d) $[(9.276)^2 \times (273.1)^3]^6$ | |
| (b) $(8.234 \div 0.002913)1023$ | | (e) $(3.985 \times 8.263)^{1/2} \div (9.623)^3$ | |
| (c) $[(3.141)^{1/2} \times (298.1)^{1/3}]^6$ | | <i>Ans.</i> 0.006439. | |
| <i>Ans.</i> 2.754×10^6 . | | (f) $(2.345 \times 9.213 \times 7.623)^{1/3}$ | |

5. Work the following, using a slide rule.

- (a) Locate on the *D* scale: 125.0, 98.1, 2.73, 292, 5.14, 0.0826, 1985. (e) $502 \times 527 \div 402 =$ (Use only one setting, by doing the division first.)
- (b) $0.01234 \times 276 =$ *Ans.* 3.41. (f) $\sqrt[3]{(973)^2 \times 243} =$ *Ans.* 613.
- (c) $0.00296 \div 273 =$ (g) $(425 \times 0.0293 \times 3.261) \div (391 \times 273 \times 3.105) =$
- (d) $(273)^2 \times 0.00891 =$ *Ans.* 664. (h) $(1110)^{1/4} =$ *Ans.* 5.77.

Section 3B

1. Solve the following equations for positive, real values of x , and check all answers.

- (a) $2x^2 + 3x - 5 = 0$ *Ans.* 1. (e) $\frac{x^2(x + 0.100)}{(0.500 - x)} = 1.46 \times 10^{-8}$
- (b) $3x(x + 0.010) = 1.0 \times 10^{-8}$ *Ans.* 2.7×10^{-4} .
- (c) $x^2(x + 0.010) = 1.0 \times 10^{-12}$ *Ans.* 1.0×10^{-5} .
- (d) $2x^2(4x + 0.10) = 253$ (f) $\frac{(x + 0.0100)}{(x^2 + 0.500)} = 0.0500$

4 CHEMICAL PRINCIPLES FUNDAMENTAL TO QUANTITATIVE ANALYSIS

4A. OUTLINE OF PRINCIPLES

Listed below are those topics of elementary chemistry that are essential to the study of quantitative analysis. The laws of stoichiometry and the composition of solutions are not reviewed in this chapter, for they may easily be found in elementary texts. The remaining topics in the outline are reviewed from the analytical chemical viewpoint. Problems on each topic are given at the end of this chapter. If there is difficulty with any topic or its problems, a review with the help of a good elementary text is in order.

- I. Laws of stoichiometry
 - A. Atomic and molecular weights
 - B. Quantitative interpretation of chemical formulae and equations
 - C. Weight problems
 - 1. Concept of the mole; its use in working problems
 - 2. Calculations from chemical equations
- II. Composition of solutions
 - A. Quantitative expressions of composition, especially molarity and weight percentage
 - B. Problems concerning composition of solutions
- III. Electrolytes. Ionic equations (p. 23)
- IV. Chemical equilibrium (p. 24)
- V. Rate of reaction (p. 30)

TABLE 4.1
STRENGTH AND SOLUBILITY OF SOME COMMON ELECTROLYTES

STRONG ELECTROLYTES		WEAK ELECTROLYTES*	
Soluble	Insoluble†	Soluble	Insoluble
SALTS			
All nitrates acetates chlorates	All sulfides except those of Li, Na, K, NH ₄ , Mg, Ca, Ba	All halides, cyanides, and thiocyanates of Zn, Cd, and Hg (II)	
All salts of Li, Na, K, NH ₄	← except { All carbonates phosphates borates chromates arsenates sulfites		
All chlorides bromides iodides	except those of → { Pb Ag Hg(I)	and except those of → { Hg(II) Cd Zn Sn(II) Sn(IV)	
All sulfates	except those of → { Ca Ba Pb Hg(I)		
ACIDS			
HCl, HBr, HI, HClO ₃ , HBrO ₃ , HIO ₃ , HClO ₄ , H ₂ SO ₄ , HNO ₃	← except { Common inorganic acids	and except H ₂ SiO ₃	Most organic acids
BASES			
LiOH NaOH KOH Ba(OH) ₂	← except { Most inorganic bases	NH ₃ Most organic bases	

*Ionization constant applies.

†Solubility product applies.

4B. ELECTROLYTES AND IONIC EQUATIONS

4B.1. Strength and Solubility of Electrolytes

Electrolytes are substances that ionize and conduct an electric current when dissolved in water. *Strong electrolytes* exist predominantly in the ionized state in dilute solutions, whereas *weak electrolytes* exist predominantly in the un-ionized state. The adjectives "strong" and "weak" are not used to describe the concentration of solutions. *Concentrated* solutions contain relatively high concentrations of solute, whereas *dilute* solutions contain only relatively low concentrations.

Two other terms need definition: soluble and insoluble. A substance is said to be *soluble* if its saturated solution contains more than 0.01 mole per liter. Although no substance is completely insoluble, those substances having solubilities less than 0.01 mole per liter are classed as *insoluble* or slightly soluble.

Table 4.1 classes some of the common electrolytes according to strength and solubility. In spite of its apparent oversimplification and incompleteness, this table is useful to the beginner and should be memorized. The information is necessary in writing ionic equations. Furthermore, the common substances are classed in groups for which the solubility-product and ionization-constant expressions apply. It should be realized that some substances fall between the groups, but to designate them would increase the complexity of the table. The student may fill in these details as his chemical knowledge increases.

4B.2. Ionic Equations

Reactions that occur in aqueous solution are best represented by ionic equations. To write an equation ionically, the formulae of the participating substances are written so as to indicate the states of the substances as well as possible. The following conventions are used.

1. Precipitates or insoluble substances are indicated by a downward arrow following the formula, or by the formula underlined: $\text{AgCl} \downarrow$ or AgCl .

2. Gases that are lost from the system are indicated by an upward arrow following the formula, as $\text{SO}_2 \uparrow$. However, that part of a gaseous substance that is dissolved in solution is treated as an ordinary solute (see 3).

3. Electrolytes are written in the form in which they exist predominantly. Thus strong electrolytes are written in the ionized form ($\text{Na}^+ + \text{Cl}^-$), while weak ones are written in un-ionized form (HCN). Perfect representation is not always possible, and it is sometimes necessary

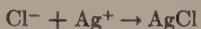
to compromise. Occasionally it may be desirable to use the formula of a nonpredominant species for clarity.

4. Any substance that exists in the same state on both sides of the equation really does not undergo reaction and is dropped from the final equation. Catalysts, etc., may be placed in parentheses above the arrow.

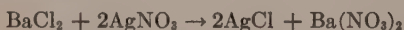
Example 1. Ionically, the reaction between BaCl_2 and AgNO_3 is



or



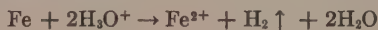
Non-ionically, the reaction is



Example 2. The ionic equation for the dissolution of $\underline{\text{Ag}_2\text{CrO}_4}$ in water is



Example 3. Ferrous ion is formed when Fe metal is dissolved in dilute H_2SO_4 . In the presence of air, oxygen oxidizes the ferrous ion to ferric. The process is represented by ionic equations as follows:



4C. CHEMICAL EQUILIBRIUM

The analytical chemist is interested in driving certain reactions as far as possible toward completion, so that they may be suitable for quantitative determinations. In other applications, it may be desirable to prevent interfering reactions. Equilibrium theory is therefore an important part of the study of analytical chemistry.

4C.1. Description of Chemical Equilibrium

No reaction is ever complete. When two reactive substances are mixed, they begin to react. At the instant of mixing, no products are present, but these soon build up in concentration. As soon as the concentrations of the products become appreciable, they react to re-form the reagents.

As the reaction proceeds, the concentrations of the reagents decrease, and therefore so does the rate at which they react; the concentrations of the products increase, and therefore so does the rate at which they react. Eventually, a state of *equilibrium* is reached, wherein the rate

of the forward reaction (between the reagents A and B) is balanced by the rate of the back reaction (between the products C and D). This state of affairs is represented by the equation



The state of equilibrium is not static, but dynamic. Each substance is being constantly used up and re-formed. At equilibrium the rate of formation of each substance equals its rate of consumption, and there is no net change in concentration.

Because the rates of the forward and back reactions are equal at equilibrium, it does not follow that the concentrations of reagents and products are equal. The rate at which substances react is highly dependent upon the specific nature of the substances. Thus A and B might have a much greater tendency to react than C and D, in which case they would be present at much lower concentrations than C and D at equilibrium, when the rates are equal.

4C.2. Displacement of Equilibrium

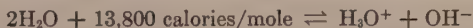
If a stress is applied to a system in equilibrium, the equilibrium tends to shift in a direction to neutralize the stress, according to *Le Châtelier's principle*. The effect of a stress is to displace, or shift, the equilibrium. By a suitable choice of stresses, the chemist may displace an equilibrium in whichever direction he desires. There are two general ways of applying stress to aqueous chemical equilibria: by heat and by concentration.

4C.2a. Effect of heat. Suppose that A and B react with the liberation of heat,



Any system containing A, B, C, and D in equilibrium may be driven to the right by removing heat (i.e., decreasing temperature), for the equilibrium shifts to the right to supply heat. Conversely, the equilibrium is shifted to the left by an increase in temperature.

Example. Water is a very weak electrolyte, which ionizes according to the equation



At 25°C the ionization is very slight, so that the molar concentrations of hydrogen and hydroxyl ions are each only $10^{-7} M$. By increasing the temperature to 100°C, the degree of ionization is increased more than sevenfold.

4C.2b. Effect of concentration. If the concentration of any substance involved in the equilibrium is changed, the equilibrium shifts to overcome, or oppose, this change. For example, in Eq. 4.1 any increase in concentration of C or D or any decrease in concentration of A or B

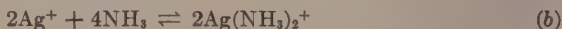
results in a shift to the left. This is the means most frequently employed by the analytical chemist to drive reactions in a desired direction.

The concentration of a particular species involved in an equilibrium system may be changed in the following ways. (1) It may be increased by addition of an excess. (2) It may be decreased by adding a substance that converts the species in question into a complex ion, precipitate, or a gas that is allowed to escape.

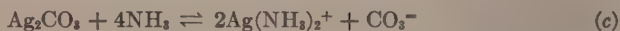
Example. Ag_2CO_3 is a slightly soluble, strong electrolyte. The saturated solution is very dilute, and the solute is completely ionized. The equation that represents the equilibrium is



Formation of a soluble complex. When NH_3 is added to the system, Ag^+ is converted to the soluble complex $\text{Ag}(\text{NH}_3)_2^+$. This decreases the concentration of Ag^+ to such an extent that the Ag_2CO_3 dissolves.



By the addition of Eqs. *a* and *b*, the over-all equation becomes



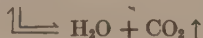
Formation of a precipitate. If an excess of a soluble iodide is added, such as NaI , insoluble AgI is formed, and the Ag_2CO_3 disappears by metathesis to AgI .



Adding Eqs. *a* and *d* gives



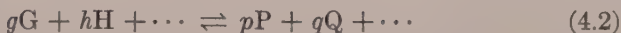
Formation of a gas. If an acid is added, slightly ionized H_2CO_3 is formed and carbonate is removed, which causes a shift of Eq. *a* to the right. In turn, H_2CO_3 breaks down into CO_2 , a gas that is lost to the atmosphere. The solubility of Ag_2CO_3 is therefore increased by the acid. The equations are



4C.3. Equilibrium Constants

Le Châtelier's principle allows a qualitative prediction of the effect of stress on an equilibrium; that is, it tells in what direction the equilibrium is shifted by a stress, but not how far. Through use of the equilibrium constant it is possible to secure quantitative information about a chemical equilibrium, and to predict not only in what direction a particular change in concentration will shift an equilibrium, but also how far it will be shifted.

4C.3a. The law of chemical equilibrium. The *equilibrium constant* for the reaction



is defined as

$$K = \frac{[P]^p [Q]^q \cdots}{[G]^g [H]^h \cdots} \quad (4.3)$$

The bracketed quantities represent molar concentrations of the solute species within the brackets, each concentration being raised to a power identical with the coefficient of that species in the chemical equation for the reaction. If a particular species is bound in any form other than that which reacts in the chemical equation, then the portion bound does not contribute to the concentration of that species in Eq. 4.3. Examples are given below.

Equation 4.3 is a quantitative expression of the law of chemical equilibrium, one of the most important of chemical principles. In any system containing G, H, ..., P, Q, ... at equilibrium, the designated function of the concentrations is always a constant numerical value. If any concentration is changed, the others spontaneously readjust (by a shifting of the equilibrium) to new values such that the function of concentrations designated in Eq. 4.3 still has the same constant value, K .

4C.3b. Factors affecting the equilibrium constant. Even for a particular reaction, the value of the equilibrium constant is dependent upon several factors, and several conditions are necessary for Eq. 4.3 to apply accurately.

1. The value of K depends upon the specific reaction and the specific substances involved. For different reactions, K may vary from immeasurably small values to immeasurably large ones.

2. Equation 4.3 is valid only when the system in question is at equilibrium. Obviously, before this point is reached, the function of concentrations in the equation may assume any value up to K . For example, at the instant of mixture of the reagents and before any products are formed, the value of the function is zero. As reaction proceeds, the value of the function changes continuously with time, attaining the value K when equilibrium is reached.

3. For a particular reaction, K usually depends upon temperature. Thus whenever a value of K is stated for a particular reaction, a corresponding temperature must be specified. If the temperature is not specified, it must be found or deduced from the context. The dependence of K upon temperature varies from one reaction to another. For some reactions, K may increase rapidly with increase in temperature (as in the ionization of water); for other reactions, K may decrease rapidly

with increase in temperature (as in the association of hydrogen and hydroxyl ions to form water); for still other reactions, K may be quite invariant with temperature.

4. The value of the equilibrium constant for a particular reaction is regarded as independent of the concentrations of the reacting substances and of other solutes in aqueous solutions, and its principal usefulness lies in this fact. However, this is only approximately true. Actually, the equilibrium constant for a particular reaction approaches constancy only as the total ion concentration in solution becomes vanishingly small. Such a law, which holds increasingly well as certain limiting conditions are approached, is called a "limiting law." Fortunately, deviations from the law of chemical equilibrium as expressed in Eq. 4.3 are not serious, even for electrolyte concentrations up to 0.1 M . It may be assumed for the purposes of quantitative analysis that this equation holds with sufficient accuracy in such dilute solutions, and that K is independent of electrolyte concentration. For greater accuracy, a different property of the solute species, called the *activity*, is substituted for molar concentration in Eq. 4.3. This concept is discussed in greater detail in Chapter 11, in connection with the solubility product. When activities are used instead of molar concentrations, Eq. 4.3 becomes exact. The activity is related to the molarity of a solute species, but the relationship is not a simple one.

4C.3c. Equilibrium constants for certain types of reactions

The solubility product. If an insoluble, strong electrolyte is dissolved in aqueous solution, the general chemical equation is



and the equilibrium-constant expression for this reaction is

$$K = \frac{[B]^n[A]^m}{[B_nA_m]_{\text{(solid)}}}$$

$[A]$ and $[B]$ represent molar concentrations of these ions in solution. $[B_nA_m]_{\text{(solid)}}$, the number of moles per liter of B_nA_m in solid B_nA_m , is constant. This term may therefore be incorporated along with K into a new constant, called the "solubility product," K_s .

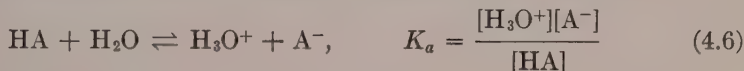
$$K_s = [B]^n[A]^m \quad (4.5)$$

Expression 4.5 has all the limitations of the general equilibrium expression, 4.3, and, in addition, it holds only for the class of insoluble, strong electrolytes (see Table 4.1). The properties and applications of the solubility-product expression are discussed in Chapter 11.

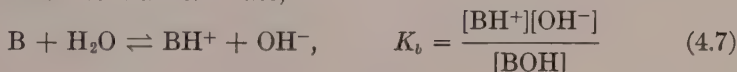
Whenever a solid takes part in an equilibrium, and when the system

is saturated with respect to such a solid, the equilibrium-constant expression is written with the (constant) concentration of the solid automatically incorporated into the equilibrium constant.

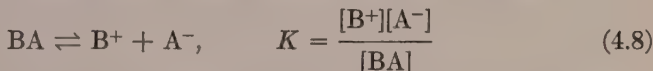
The ionization constant. When a weak electrolyte, BA, dissolves in water, the chemical equation is $BA \rightleftharpoons B^+ + A^-$, and the equilibrium constant for this reaction is given the special name "ionization constant," or "dissociation constant." If the substance is a weak acid,



If the substance is a weak base,



There are a few salts that are weak electrolytes, and for these



Equations 4.6 to 4.8 are subject to all the limitations of the general equilibrium expression, and, in addition, they hold only for weak electrolytes (see Table 4.1). It is easy to understand how these equations lose meaning with strong electrolytes, which are completely ionized in dilute solution, and for which the concentration of undissociated solute approaches zero in dilute solutions. In these cases, the concentration functions in Eqs. 4.6 to 4.8 become meaninglessly large. Ionization constants are discussed in detail and quantitatively applied to acid-base equilibria in Chapter 17.

The ion product of water. Water is a weak electrolyte and ionizes according to the equation



In all dilute aqueous solutions with solute concentrations less than a few tenths molar, the molar concentration of water is practically constant, lying between 55.0 and 55.5 *M*. (For proof, work Prob. 1, Sec. 4C, p. 36.) As such a constant, $[H_2O]$ may be incorporated into K , giving a new constant called the "ion product of water," K_w .

$$[H_3O^+][OH^-] = K_w = 1.0 \times 10^{-14} \quad (25^\circ C) \quad (4.9)$$

The implications and consequences of this equation are discussed in detail in Chapter 18.

Solid-gas equilibria. See Chapter 10.

Redox equilibria. See Chapter 19.

4D. RATE OF REACTION

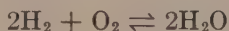
It is necessary to distinguish clearly between the *tendency* of the reagents to react and reach a certain state of equilibrium, and the actual *rate* at which they react to reach that state of equilibrium. In general, there is no relation between the tendency and the rate. Thus, in Eq. 4.2, the tendency of G, H, . . . to react might be very great, and the state of equilibrium might lie far to the right. But if the rate at which G, H, . . . react is very low, equilibrium might not be reached in the time allowed for the process.

The consideration of reaction rate is of great importance in analytical chemistry, and is encountered frequently. In volumetric analysis, for example, standard solution is added in small increments as the end point is approached. If the reaction rate is not high, too long a wait is required for reaction after each increment is added. Several good volumetric methods are based upon reactions that would normally be too slow to be practical, but may be speeded up with a catalyst. (An example is the reaction between arsenite and permanganate, catalyzed by a trace of iodide.)

4D.1. Equilibrium and Rate

There are many reactions whose states of equilibrium are far to the right, but whose rates are negligible. A few common examples are discussed briefly in this section.

1. The equilibrium



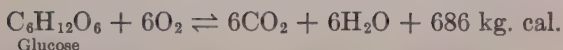
lies far to the right at room temperature. However, mixtures of hydrogen and oxygen gas are "stable" at room temperature simply because the reaction rate is negligible. With finely divided Ag, Au, or Pt as a catalyst, this reaction may be made to proceed in a controlled manner at room temperature.

2. Another important reaction whose state of equilibrium is far to the right is



All the reagents are present in sufficient amount in the atmosphere and oceans so that, if equilibrium were reached, the oceans would be 0.1 *M* in nitric acid, and the oxygen would be virtually gone from the atmosphere. This reaction, although negligible under ordinary conditions, is brought about by nature in devious ways, and is known as the "fixation of nitrogen." Man has catalyzed this reaction in the Ostwald process.

3. The oxidation of glucose (and many other organic compounds) is still another example for which the equilibrium state is far on the side of the oxidation products at room temperature.



Yet, glucose is stable in air, the rate of oxidation being negligible. Living organisms contain catalysts (enzymes) which bring about the oxidation of glucose in a controlled way to provide heat and energy for the organisms. Were the uncatalyzed rate of oxidation of glucose significant, the forms of life that we know would be unable to exist on earth.

4D.2. Factors Affecting Rate

1. An increase in temperature often increases reaction rate greatly; a rise of 10°C will double the rate for many reactions. For example, even with a catalyst, it is still necessary to carry out the Ostwald process at an elevated temperature to bring about fixation of nitrogen at an economical rate.

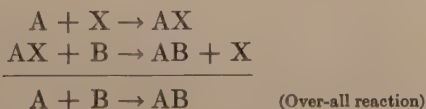
The extent to which a reaction rate may be increased by raising the temperature is sometimes limited, for the equilibrium may be adversely affected. This is the case in the Haber process for the production of NH_3 from the elements, which is an exothermic reaction.



The elements react very slowly at low temperatures. The rate of reaction may be increased by raising the temperature, but then the extent of reaction is decreased, for the equilibrium is displaced to the left. This is why a catalyst, rather than an indiscriminately high temperature, must be used to increase the rate.

2. The reaction rate is increased by raising the concentrations of the reagents. An increase in concentration of reagents has no effect on the value of K (Eq. 4.3), but the equilibrium is displaced to the right in accordance with Le Châtelier's principle.

3. A *catalyst* increases the rate of reaction. A negative catalyst decreases the rate of reaction. A catalytic substance is not changed permanently by the reaction; but the catalyst does enter the reaction to form intermediate substances that react readily and are broken down in the course of the reaction to re-form the catalyst. The following equations illustrate one way in which a catalytic substance, X , may change the rate of reaction of two reagents, A and B , without itself being permanently changed.



Although a catalyst increases the rate of reaction and the rate at which the system approaches equilibrium, it does not change the point of equilibrium, for both the forward and the reverse reactions are catalyzed to the same extent.

4. A slow reaction may be speeded (i.e., induced) by the occurrence of another reaction. Suppose that A and C alone do not react at an appreciable rate, and that A and B alone do react. If it is found that A and C do react in a system containing B, then the reaction between A and C is said to be *induced* by the reaction between A and B. A is called the *actor*, since it acts on both B and C. B is called the *inductor*, and C is the *acceptor*. The primary reaction is $A + B$, and $A + C$ is the induced reaction.

The induced mechanism is definitely different from catalysis. Thus B cannot be a catalyst, since it is used up in the reaction. The induction occurs through reactive intermediates formed in the primary reaction, in the same way that catalysis does, but the inductor is not re-formed. Induced reactions have been recognized for over a hundred years, but definite mechanisms have not been suggested until recently (L2, M12).

Induced reactions may be extremely important as sources of error in quantitative determinations. As a specific example, permanganate does not react at an appreciable rate with chloride in dilute acid solution. On the other hand, ferrous ion is stoichiometrically titratable with standard permanganate in dilute acid solution. In the presence of chloride, however, the stoichiometry is upset, since the oxidation of chloride by permanganate is induced by the reaction between permanganate and ferrous ion. Without proper precautions, errors of several per cent may occur. Induced reactions may cause errors of hundreds of per cent in the titration of peroxides with ferrous ion.

5. The rate of reaction between solid materials may be increased by more intimate contact between the reagents. Powdering and mixing the reagents well before reaction increase the contact surface. Stirring during reaction also increases the degree of contact and thus the rate. These measures have no effect upon the equilibrium. If the reaction may be carried on at a high enough temperature to melt one or more of the reagents, the efficiencies of contact and stirring are greatly increased; this is the basis of opening a sample by fusion with a flux (p. 115).

QUESTIONS

Section 4A

1. State the laws of definite and combining proportions, and describe specifically how they are utilized in the gravimetric analysis of a sample for chloride by precipitation as silver chloride.

2. Define oxidation number. Write the formulae of the following compounds: aluminum chloride, phosphoric acid, calcium acetate, chromic sulfate, zinc phosphate, ceric nitrate, manganic chloride, potassium thiocyanate, ferric ferrocyanide, aluminum arsenate.

3. Outline the steps in writing a chemical equation, and illustrate with the reaction of calcium chloride on silver nitrate to precipitate insoluble silver chloride.

4. What is the international table of atomic weights?

5. Define the mole and tell why this unit is used by chemists.

6. Criticize the statement, "A mole of a substance is the molecular weight in grams."

7. Write balanced equations for the following reactions:

- | | |
|--|--|
| (a) Sodium sulfate + calcium chloride | (f) Phosphoric acid + ammonia |
| (b) Aluminum nitrate + ammonia | (g) Sodium oxalate + barium chloride |
| (c) Lead acetate + hydrochloric acid | (h) Potassium ferrocyanide + ferric chloride |
| (d) Calcium carbonate + nitric acid | (i) Sodium arsenate + silver nitrate |
| (e) Hydrogen sulfide + cupric chloride | (j) Sodium nitrite + sulfuric acid |

8. The element A forms APO_4 , and the element B forms Ag_2B . Write formulae for: A sulfate, aluminum B, a compound of A and B.

9. Define molarity.

10. For what sorts of solutions may the volume concentrations (in grams of solute per 100 ml of solution) be taken as numerically equal, within a per cent or two, to the weight concentrations (in grams of solute per 100 g of solution)?

11. Define and compare density and specific gravity.

12. Describe units of concentration other than those based upon the weight of solute per unit volume or per unit weight of solution, and suggest applications in which these units might prove useful.

13. What exceptions are there to the law of definite proportions? Explain why these exceptions seldom cause error in the analysis of natural substances.

Section 4B

1. Classify the following electrolytes according to strength and solubility. BaSO_4 , NaNO_3 , CaCl_2 , ZnCO_3 , $\text{Cu}(\text{OH})_2$, HClO_4 , H_3PO_4 , Hg_2Cl_2 , Ag_2CrO_4 , H_2S .

2. What is meant by the statement that CaSO_4 is a strong electrolyte that forms a very dilute saturated solution?

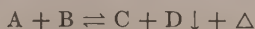
3. Making use of the information in Table 4.1 (p. 22), write ionic equations for reactions between the following pairs of substances. Where there is no reaction, indicate "N.R."

- | | |
|--|--|
| (a) Cupric chloride and sodium sulfide | (h) Magnesium chloride and silver sulfate |
| (b) Hydrochloric acid and zinc sulfide | (i) Barium hydroxide and copper sulfate |
| (c) Ammonium nitrate and sodium hydroxide | (j) Ferric sulfate and sodium phosphate |
| (d) Acetic acid and lead nitrate | (k) Nickel nitrate and sodium carbonate |
| (e) Sodium chloride and potassium sulfate | (l) Zinc iodide and mercurous nitrate |
| (f) Sulfuric acid and barium chlorate | (m) Perchloric acid and sodium carbonate |
| (g) Mercuric nitrate and aluminum chloride | (n) Aluminum sulfate and ammonium arsenate |
| | (o) Stannous chloride and sodium phosphate |

Section 4C

1. In a gravimetric analysis, a sought-for substance B is converted to a product

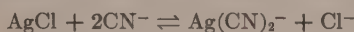
D, which is weighed. What measures might be used to make the conversion as complete as possible?



2. Why is the precipitation of AgNO_3 by NaCN not complete in acid solution? Explain how the acidity should be altered to give more complete precipitation.

3. Using ionic equations, explain why CuCO_3 is soluble in dilute acid, even though it is insoluble in water.

4. AgCl is soluble in aqueous KCN , according to the reaction



Write the equilibrium constant for this reaction. Using Le Châtelier's principle, and also using the equilibrium-constant expression, explain the effect of an increase in $[\text{CN}^-]$ on the solubility of AgCl .

5. Write equilibrium constants for the following equilibria.

- (a) $\text{ZnS} + 2\text{H}_3\text{O}^+ \rightleftharpoons \text{H}_2\text{S} + \text{Zn}^{2+} + 2\text{H}_2\text{O}$ (f) $\text{BaCrO}_4 + \text{H}_3\text{O}^+ \rightleftharpoons \text{Ba}^{2+} + \text{HCrO}_4^- + \text{H}_2\text{O}$
 (b) $\text{Hg}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{HgCl}_2$ (g) $\text{NH}_4^+ + \text{OH}^- \rightleftharpoons \text{NH}_3 + \text{H}_2\text{O}$
 (c) $\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$ (h) $\text{Hg}_2\text{Cl}_2 \rightleftharpoons \text{Hg}_2\text{Cl}^+ + \text{Cl}^-$
 (d) $\text{H}_3\text{O}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{HCO}_3^- + \text{H}_2\text{O}$ (i) $\text{BaSO}_4 + \text{CO}_3^{2-} \rightleftharpoons \text{BaCO}_3 + \text{SO}_4^{2-}$
 (e) $\text{AgCN} + \text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$ (j) $\text{Al}(\text{OH})_3 + \text{OH}^- \rightleftharpoons \text{AlO}_2^- + 2\text{H}_2\text{O}$

6. Give an example of a reaction having an equilibrium constant which is: (a) large, (b) small, (c) of the order of unity.

Section 4D

1. What is wrong with the following statement? "If an equilibrium lies far to the right, the reaction goes completely." Give examples for which this statement is false.

2. If a reaction has a certain rate at 25°C , approximately how much faster would it be at 100°C ?

3. Give a specific example of a chemical reaction that is accelerated by a catalyst, and describe the mechanism.

4. In the reaction between Fe^{2+} , Cl^- , and MnO_4^- (p. 32), balance and name the primary and induced reactions. Also name the actor, inductor, and acceptor.

PROBLEMS

Section 4A

1. Summarize the information given in the formula AlPO_4 .

Ans. Atom ratio: $\text{Al}:\text{P}:\text{O} = 1:1:4$. Composition:
22.1245% Al; 25.3982% P; 52.4773% O.

2. Summarize the information given in the equation



3. Element A forms the compound ACl_n , and B forms Ag_mB . Write the formula for a compound between A and B. *Ans.* A_mB_n .

4. Give an expression for the oxidation number (a) of element A in terms of the oxidation number (b) of element B, knowing that they form the compound B_nA_m .

5. Calculate the percentage of: Rb in RbNO_3 ; Fe in Fe_2O_3 ; H_2O in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$;

CaO in CaCO_3 ; SO_3 in H_2SO_4 ; N_2O_5 in HNO_3 .

Ans. 69.944% Fe in Fe_2O_3 ;
56.03% CaO in CaCO_3 .

6. Calculate the weight of insoluble PbS obtained by the action of excess H_2S on 0.287 g $\text{Pb}(\text{NO}_3)_2$.

7. Calculate the weight of CuI produced by the action of excess KI on 0.583 g CuSO_4 , according to the equation



Ans. 0.696 g.

8. Calculate the weight of iodine produced by the action of excess KI and H_2SO_4 on 2.97 g KMnO_4 , according to the equation



9. After decomposition, the Cl in 0.5000 g of an organic compound is converted quantitatively to AgCl, of which 0.402 g is obtained. What is the % Cl in the compound?

Ans. 19.89%.

10. How much K_2CrO_4 is needed to react with 0.692 g $\text{Pb}(\text{NO}_3)_2$ to form insoluble PbCrO_4 ? How much PbCrO_4 is formed?

11. The Ca in a sample is precipitated and quantitatively recovered as the oxalate, which yields 0.470 g CaO after ignition. How much Ca is in the sample?

Ans. 0.336 g.

12. What weight of Na_2O is contained in 0.200 g Na_2CO_3 ?

13. What is the per cent of sulfur in a sample made by mixing 1.00 g CaSO_4 with 4.00 g BaSO_4 ?

Ans. 15.70%.

14. How much CO_2 is obtained by treating 49.1 g Na_2CO_3 with excess H_2SO_4 , and then heating to boil off the gas?

15. A 0.100-g sample contains 40.0% Na_2SO_4 and 20.0% K_2SO_4 as the only sulfates. Calculate how much BaSO_4 may be obtained after excess BaCl_2 is added to the sample.

Ans. 0.0925 g.

16. A 0.153-g sample contains Na_2SO_4 and K_2SO_4 only. What is the composition of the sample, if 0.245 g BaSO_4 is obtained by the addition of excess BaCl_2 ?

17. What weight of CaCl_2 must be taken to give the same yield of AgCl as 0.335 g NaCl?

Ans. 0.318 g.

18. A 1.00-g sample contains 60.0% $\text{X}(\text{NO}_3)_2$ and 40.0% XCl_2 . Complete precipitation of all the chloride gives 0.7290 g AgCl. Find the atomic weight of the divalent element, X.

19. Calculate the milliliters of NH_3 solution (sp. gr. 0.960) containing 9.91% NH_3 by weight required to precipitate the aluminum from 2.00 g of alum, $\text{KAl}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$.

Ans. 2.27 ml.

20. How much H_2SO_4 is obtained by the combination of 11.9 g SO_3 with excess water?

21. Devise factors for converting:

(a) Molarity of HNO_3 to milligrams of HNO_3 per 250 ml of solution.

Ans. 1.58×10^4 .

(b) Grams of solute per liter of solution to ounces of solute per quart of solution.

(c) Grams of solute per liter of solution to percentage composition by weight, using the density, D , of the solution.

(d) Percentage composition by weight to grams of solute per liter of solution, using the density, D , of the solution.

Ans. 10*D*.

22. Calculate the molar concentrations of the following concentrated reagents.

(a) 36% HCl; density, 1.18 g/ml.

Ans. 11.6 *M*.

(b) 95% H_2SO_4 ; density, 1.83 g/ml.

- (c) 28% NH_3 ; density, 0.90 g/ml.
 (d) 99.5% acetic acid; density, 1.057 g/ml.
23. How many grams of each solute are there in the following solutions?
 (a) 175.0 ml of 0.76 M NaCl . *Ans.* 7.8 g.
 (b) 763 ml of 0.17 M H_2SO_4 .
 (c) 196.0 ml of 0.43 M $\text{Al}_2(\text{SO}_4)_3$.
 (d) 76.3 ml of 0.193 M NaOH .
 (e) 179 ml of 0.213 M H_3PO_4 .
24. Give the molar concentrations of the following solutions:
 (a) 1.34 g $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ in 150 ml of solution. *Ans.* 0.0366 M .
 (b) 21.0 g 95% H_2SO_4 in 214 ml of solution.
 (c) 70.0 g of potassium tetroxalate ($\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) in 971 ml of solution. What are the molar concentrations of oxalate and of acid?
25. What weight of NaOH is required to react with 35.0 ml of 0.190 M H_2SO_4 ?
Ans. 0.532 g.
26. The Cu in 17.6 ml of a $\text{Cu}(\text{NO}_3)_2$ solution is precipitated quantitatively and converted to CuO , of which 0.1095 g is obtained. Calculate the molarity of the $\text{Cu}(\text{NO}_3)_2$ solution.
27. A 15.0-ml portion of an H_2SO_4 solution gives 1.753 g BaSO_4 . What is the molarity of the acid?
Ans. 0.501 M .
28. What is the molarity of an H_3PO_4 solution prepared by dissolving 29.3 g P_2O_5 in one liter of solution?
29. What weight of CaO is required to react with 14.7 ml of 0.0763 M HCl ?
Ans. 31.4 mg.
30. How much BaO would be needed to prepare one liter of 0.0557 M $\text{Ba}(\text{OH})_2$?
31. A precipitate of AgCl weighing 1.653 g is obtained after addition of excess AgNO_3 to a 50.0-ml aliquot of an HCl solution. What is the molarity of the acid?
Ans. 0.2307 M .
32. What volume of 0.0907 M NaOH is needed to react with 44.9 ml of 0.0475 M H_2SO_4 ?
33. The Na in a 0.712 M Na_2CO_3 solution is quantitatively converted to NaCl , of which 0.532 g is obtained. What volume of Na_2CO_3 solution is used?
Ans. 6.40 ml.
34. What weight of magnesium pyrophosphate ($\text{Mg}_2\text{P}_2\text{O}_7$) would be obtained if the Mg in 46.2 ml of 0.387 M MgCl_2 solution were quantitatively converted to the pyrophosphate?
35. If 53.2 ml of 0.171 M HCl are required just to neutralize 24.9 ml of $\text{Ba}(\text{OH})_2$, what is the molarity of the base?
Ans. 0.183 M .
36. What is the concentration of an H_2SO_4 solution, 24.9 ml of which are required to react with 42.6 ml of a 0.0928 M NaOH solution?
37. An aqueous solution contains 279.0 g KNO_3 per liter, and has a density of 1.162 g/ml. What is the weight percentage of KNO_3 ?
Ans. 24.01%.
38. An aqueous solution contains 30.0% KOH by weight as the only solute. Analysis of the solution shows it to be 6.90 M . What is the density?

Section 4C

1. In the *Handbook of Chemistry* (L4), find the densities of water and of 0.20 M HCl . For each of these solutions, calculate the molar concentration of the water, and show how the answer supports the assumption that $[\text{H}_2\text{O}]$ is constant for the derivation of Eq. 4.9.
Ans. 55.5; 55.2 M .

5 THE THEORY OF ERROR AND THE TREATMENT OF QUANTITATIVE DATA

Accuracy, precision, error, and the treatment of experimental data are difficult concepts to present. On the one hand, they should be taught at the beginning of the course, because the student cannot work intelligently and efficiently until he has them in mind and until he realizes what means are used to minimize error. On the other hand, an understanding of the rationale of discovering and reducing error requires more experience with quantitative laboratory work than the beginning student has.

Therefore it will not be easy to learn all parts of this chapter at once. It is suggested that sections 5A, 5B, and 5H be learned early. The remaining sections may profitably be taken up after the first few experiments have been completed.

5A. ACCURACY AND PRECISION

5A.1. Definitions

The *accuracy* of a measurement describes the difference between an observed value and the true value. The measurement is said to have high or low accuracy, depending upon whether the observed value is close to, or far from, the true value. On the other hand, the *precision* of a set of measurements on the same quantity describes the differences among the individual measurements themselves; if they are close together, the measurements have high precision; if scattered, they have low precision.

For example, suppose that a certain quantity is measured in quintuplicate by each of three different methods, A, B, and C, with the results shown in Fig. 5.1. In each set, because of experimental error, the five measurements are scattered. Method A has high precision because the individual determinations are close together, and high accuracy be-

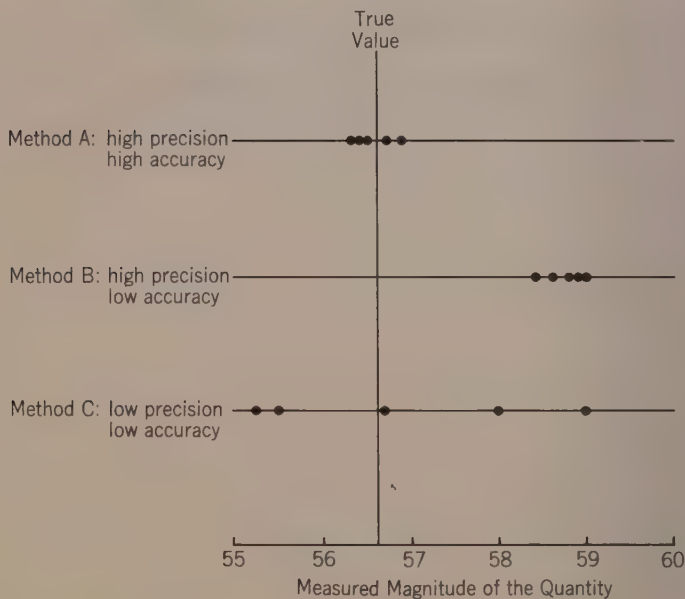


FIG. 5.1. Accuracy and Precision (Reprinted from A. A. Benedetti-Pichler, *Industrial and Engineering Chemistry, Analytical Edition*, 8, 373 [1936], Fig. 1, by permission of the publisher.)

cause the individual determinations are close to the true value. Method B has high precision, but the accuracy is low because the individual determinations are far from the true value. Method C has low precision because the determinations are far apart, and low accuracy because the determinations are far from the true value (except for an occasional lucky measurement).

5A.2. Error and Deviation

In this text the terms “accuracy” and “precision” do not have quantitative significance, and are used in a rough descriptive sense only. Instead, the terms “error” and “deviation” are quantitatively defined.

Let a set of N replicate measurements, X_1, X_2, \dots, X_N , be made on

a single quantity. Also, let the mean (sometimes called the average, or arithmetic mean) be defined as

$$\bar{X} = \frac{X_1 + X_2 + \cdots + X_N}{N} \quad (5.1)$$

This set of measurements has two interesting and useful properties.

1. For each measurement (and also for the mean) there is a finite difference between the observed value (X_i) and the true value (μ). This difference is called the *error* of the measurement.

$$\text{Error} = \text{observed value, } X_i, - \text{true value, } \mu \quad (5.2)$$

The accuracy of a measurement is expressed quantitatively by the error, which is low when the accuracy is high.

2. All the measurements are not identical, but differ appreciably from each other and are scattered. The closeness of the measurements to each other, without regard for their closeness to the true value (which may not be known), is described by the *deviation* of the group of measurements. Several different deviation measures are in common use that describe the over-all scattering of the set of measurements.

The deviation (x_i) of any single measurement from the mean is defined as the difference between that measurement and the mean.

$$x_i = X_i - \bar{X} \quad (5.3)$$

The *average deviation* (\bar{x}) of the set of measurements is the average of the individual deviations, taken without regard for sign.

$$\bar{x} = \frac{|x_1| + |x_2| + \cdots + |x_N|}{N} \quad (5.4)$$

(The vertical bars $| \quad |$ enclosing a quantity are a mathematical notation that the absolute value of the quantity is taken, without regard for sign.)

Two other useful deviation measures are the *range* (w) and the *standard deviation* (s).

$$w = X_{\text{largest}} - X_{\text{smallest}} \quad (5.5)$$

$$s = \sqrt{\frac{x_1^2 + x_2^2 + \cdots + x_N^2}{N - 1}} \quad (5.6)$$

The precision of the set of measurements is quantitatively expressed by \bar{x} , w , or s , which is low when the precision is high.

The average deviation is becoming obsolete. However, it is so ingrained and prevalent in the literature that the student must know its definition. It is recommended that w or s be used as deviation

measures, the reason being that they are statistically interpretable, while \bar{x} is not. The range w may be calculated rapidly, and is often used for small sets of measurements. If the estimate of precision is to be used in making statistical tests, however, s is the better deviation measure, since it is more efficient* than w .

It should be noted that the error of a measurement cannot be known unless the true value is known. However, \bar{x} , w , or s for a set of observations may be calculated whether the correct value is known or not. Precision does not necessarily bear any relationship to accuracy, although in certain cases it is justifiable to infer high accuracy from high precision (p. 53).

As defined in Eqs. 5.1 to 5.6, the error and deviation measures are expressed on an *absolute* basis, in the same units as the measurements themselves. However, it is often more meaningful to express error and deviation as quantities *relative* to the magnitude of the quantity being measured. Thus

$$\text{Relative error} = \frac{\text{error}}{\text{true value}} \quad (5.7)$$

$$\text{Relative range} = \frac{w}{\bar{X}} \quad (5.8)$$

$$\text{Relative standard deviation} = \frac{s}{\bar{X}} \quad (5.9)$$

These relative quantities have no units, being only ratios of two quantities measured in the same units. When multiplied by 100, 1000, or 1,000,000, these relative quantities become expressed in terms of *percentage* (%), *parts per thousand* (p.p.t.), or *parts per million* (p.p.m.), respectively.

Example. Four measurements on the weight of an object whose correct weight is 25.6 mg are: 25.1, 25.6, 25.2, 24.9 mg. The mean weight, error of the mean, and various deviation measures are calculated as follows:

Number of the Measurement, i	Observed Weight, X_i	Deviation from the Mean, x_i	x_i^2
1	25.1 mg	-0.1 mg	0.01
2	25.6	0.4	0.16
3	25.2	0.0	0.00
4	24.9	-0.3	0.09
	<hr/> 4 100.8	<hr/> 4 0.8	<hr/> 0.26
	$\bar{X} = 25.2 \text{ mg}$	$\bar{x} = 0.2 \text{ mg}$	
$w = 25.6 - 24.9 = 0.7 \text{ mg, or}$			
$\text{relative } w = \frac{0.7 \text{ mg}}{25.2 \text{ mg}} = 0.028, \text{ or } 2.8\%, \text{ or } 28 \text{ p.p.t.}$			

*The more efficient a statistical quantity, the more reliably it may be estimated from a given number of measurements.

$$s = \sqrt{\frac{0.26}{4-1}} = 0.29 \text{ mg, or}$$

$$\text{relative } s = \frac{0.29 \text{ mg}}{25.2 \text{ mg}} = 0.012, \text{ or } 1.2\%, \text{ or } 12 \text{ p.p.t.}$$

$$\text{Error of the mean} = 25.2 - 25.6 = -0.4 \text{ mg, or}$$

$$\text{relative error} = \frac{-0.4 \text{ mg}}{25.6 \text{ mg}} = -0.016, \text{ or } -1.6\%$$

5A.3. Reporting the Result of a Measurement

If a series of measurements is made on a quantity, it may be shown that the mean is probably more correct than any single, randomly chosen measurement in the series. Hence the mean is reported. However, a quantity has little significance unless it is accompanied by an estimate of the precision; hence the mean should be accompanied by a precision measure, preferably s or w . Finally, the reliability of the mean depends on the number of measurements, which should also be reported. These three items are the minimum information that must be reported (A10). As an example, the mean weight of the object in the above example should be reported as 25.2 mg (mean of four determinations; $s = 0.29$ mg). Because different deviation measures exist, the one actually used must be specified or understood. Thus it is not sufficient to report the foregoing mean length as 25.2 ± 0.29 mg, because this does not reveal whether the deviation measure is \bar{x} , s , or w .

5A.4. Purpose of the Study of Error

Although it can never be entirely eliminated, experimenters strive constantly to reduce error. A formal and quantitative study of error yields general principles and methods that are very helpful in (1) revealing sources of error, (2) testing the effectiveness of a given attempt to reduce error, (3) computing properly, and (4) estimating how close an observed value falls with respect to the true value. These principles are of great importance, and occasion for their application arises in all branches of science, wherever measurement is involved. Some of these principles and their application are described qualitatively in the remainder of this chapter. A more quantitative treatment may be found in the Supplement.

5B. RANDOM AND DETERMINATE ERROR

Errors are classified as either random or determinate. A *random error* is one that varies nonreproducibly from one measurement of a set

to the next, and is not of the same magnitude for any two measurements of the set, except by chance. Random errors are also called *statistical* or *indeterminate* errors. A *determinate* error is one that affects every measurement of a set to the same extent, and remains fixed throughout all the measurements. In Fig. 5.1 (p. 38) the errors of Methods A and C are predominantly random, whereas the errors of Method B are largely determinate.

As a specific example, suppose that a series of measurements is made on the length of a board, to the nearest 0.1 cm, using a linen tape graduated in centimeters. The following errors vary with each determination, and are random, each contributing to a scattering of the individual determinations. (1) Failure to align the ends of the tape and board perfectly. (2) Failure to estimate correctly the nearest tenth of a division on the tape. (3) Variation in tension on the tape as it is stretched along the board. On the other hand, if the tape is old, and has become permanently stretched through use so that it reads several tenths of a centimeter less than the true length of the board, this error is determinate, since it is the same in all of the determinations.

It is important to realize that the foregoing classification is an ideal one. In practice, any real error is a composite, contributed to by several sources, some of which may be random and some determinate. By statistical methods it is possible to resolve an observed error into a random part and a determinate part, and this separation aids in the discovery and reduction of the component errors.

5C. THEORY OF RANDOM ERROR. STATISTICS

5C.1. Distribution of Measurements. The Error Curve

Suppose that the true value of a quantity is μ , and that this quantity is measured by a certain method. If a large number of measurements is made, the individual measurements are not all identical and equal to μ , but are scattered about μ , owing to random error. Let the magnitude of any single measurement be X . Then the relative frequencies of occurrence of different-sized measurements are shown in Fig. 5.2. For each point on the curve, the ordinate represents the relative frequency (i.e., probability) of occurrence of a measurement whose magnitude is X , or whose error is $X - \mu$.* The curve of Fig. 5.2 is called a *distribution curve*, since it shows how individual measurements are distributed about the true value. More exactly, the particular curve of Fig. 5.2 is called the *normal distribution curve*, *Gaussian distribution curve*, *error curve*,

*The bottom scale of abscissae may be disregarded here. It is used principally in the quantitative treatment of the error curve (see Supplement, p. 613).

or *probability curve*. The curve is important, since it represents most classes of measurements that are of interest to the chemist, though there are some classes that are differently distributed.

Three important properties are immediately apparent on inspection of Fig. 5.2. (1) Since the curve is symmetrical, positive and negative errors are equally probable. For every positive error in a large number of measurements, there tends to be a corresponding negative error of equal magnitude. (2) Small errors occur much more frequently than

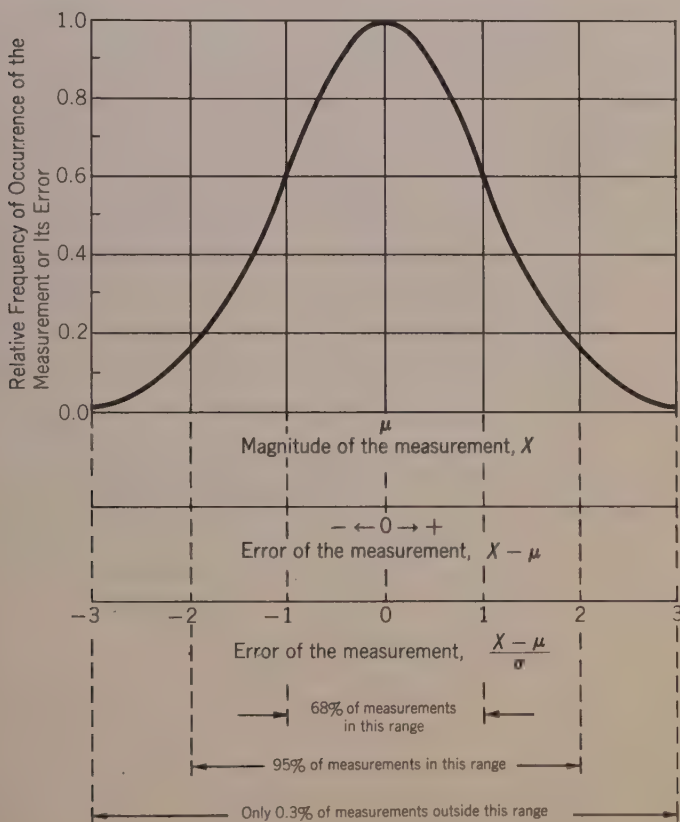


FIG. 5.2. The Normal Distribution Curve

large ones. (3) The occurrence of a large error is relatively improbable. Detailed mathematical analysis of the error curve leads to generalizations that are of help in making, treating, and interpreting measurements.

The breadth or spread of the curve indicates the precision of the measurements. A precise method of measurement gives a curve that is

sharply peaked and that drops off rapidly for large errors; for imprecise measurements, the curve is broad. The spread of the curve is determined by, and related to, the standard deviation, a relationship that is expressed in the equation for the normal curve. A quantitative description of the normal distribution is given in the Supplement (p. 613).

5C.2. General Procedure in Making Measurements

In measuring a quantity, the primary objective is to find the true value, μ . Almost always, a second objective is to find the precision of the method of measurement, which is best described by the true standard deviation, σ . Because of random error there is no assurance that a single measurement or the mean of a few measurements will give the true value, μ . Similarly, there is no assurance that the standard deviation, s , as reckoned from a small set of measurements, will be the same as the true standard deviation, σ . The values of μ and σ cannot be known exactly unless an infinite number of measurements is made. In practice this is impossible, and the worker must content himself with taking a sample of a few measurements and using this set to obtain the best possible estimates of μ and σ . *It is very important to distinguish between the sought-for true values, μ and σ , and the observed \bar{X} and s , which are taken as estimates of μ and σ .*

It is almost intuitively understandable that \bar{X} is the best estimate of μ that may be obtained from a finite set of measurements. Because of the symmetry of the error curve, positive and negative errors in the individual measurements tend to cancel in the averaging process employed to find \bar{X} . This cancellation becomes more perfect the larger the number of measurements (N) in the set, and the reliability of \bar{X} as an estimate of μ increases as N increases. However, mathematical considerations show that the reliability of \bar{X} increases only as the square root of N ; thus a point of diminishing returns is quickly reached in attempting to increase the reliability of \bar{X} simply by increasing N .

Though it is less obvious, theoretical consideration also shows that the best estimate of σ that may be made from a finite set of measurements is s . The reliability of s as an estimate of σ increases with N . Values of s computed from small sets of measurements are not very reliable estimates of σ . Typically, for $N \leq 4$, s may differ several-fold from σ .

In conclusion, when \bar{X} and s are computed from a small set of measurements, all that the worker may affirm with any degree of confidence is that the sought-for μ and σ probably fall within certain ranges about \bar{X} and s , respectively.

5C.3. Quantitative Study of Random Error

The quantitative study of random error is an aspect of statistics, and must be made mathematically. Mastery of statistics equips the student to give quantitative answers to questions of the following nature, which constantly beset the person who must make and interpret measurements. In the Supplement (pp. 620-35), elementary statistical methods are presented sufficiently to permit answers to these questions.

1. If a set of N measurements yields an \bar{X} and an s , what is the probability that the sought-for μ and σ may be assumed to fall within certain ranges about \bar{X} and s ? An answer to this question is necessary in order to express the probable errors of \bar{X} and s when taken as estimates of μ and σ .

2. If a set of N_1 measurements yields \bar{X}_1 and s_1 , and a set of N_2 measurements yields \bar{X}_2 and s_2 , just how different must \bar{X}_1 and \bar{X}_2 (or s_1 and s_2) be, in order to be judged significantly different? An answer to this question is necessary in any testing or comparison procedure. A few examples are: (a) Testing one method of analysis against another. (b) Comparison of the results of one analyst with those of another. (c) Finding if a sample meets certain specifications.

3. If the σ or s of a single measurement is known, how many measurements must be made in order that the sought-for μ may be assumed with high probability to fall within a certain range about \bar{X} ?

4. If, in a set of equally reliable measurements, one differs considerably from the others, the retention or rejection of this one may have a considerable effect on \bar{X} . How different must the discordant measurement be before it may be properly rejected?

5. How should the accuracy obtained by a student on a quantitative determination be judged?

5D. DETERMINATE ERROR

5D.1. Discovery of Determinate Error

Where determinate error exists in a set of measurements, the effect is to introduce a significant difference between the mean of the set (\bar{X}) and the true value (μ). To reveal whether the observed error of a method of analysis is predominantly determinate or random, a series of determinations is made by the method in question on a sample whose true value is known. When the difference between \bar{X} and μ is several times larger than \bar{x} , s , or w , statistical methods are not needed to decide that the error of the method is largely determinate. However, when the difference between \bar{X} and μ is of the same order of magnitude as \bar{x} , s , or

w, quantitative statistical tests must be applied to find if determinate error is significant.

5D.2. Kinds of Determinate Errors

All determinate errors are not constant, though some may be. *Systematic error* is always in one direction, but the magnitude is not reproducible and may vary from one determination to another. In the gravimetric determination of sulfate as BaSO_4 , a part of the sulfate may be coprecipitated as Na_2SO_4 instead of as BaSO_4 , making the results low. The actual extent of coprecipitation depends largely upon conditions that are difficult to control, such as temperature, rate of addition of reagents, and stirring, and varies greatly from one determination to the next. Such an error is systematic.

A *constant error*, as the name implies, is one whose absolute magnitude is constant and reproducible from one determination to the next. Such errors are quite common. In many analyses fixed amounts of some reagents are used in all determinations, regardless of the amount of sought-for substance. (Examples are the volume of indicator reagent used in titrations, volume of water used to dissolve the sample, etc.) If such a reagent contains an impurity, it will cause a constant error in all determinations. Solubility losses are often constant errors.

A *proportional error* is one whose absolute value is proportional to the amount of sought-for constituent, that is, only the relative error is constant. Such an error would be caused by an erroneous concentration of a standard solution that is used to titrate unknown samples, or by gravimetric calculations that are based on an incorrect gravimetric factor.

5E. REDUCTION OF ERROR

5E.1. General Procedure for Reducing Error

After an error is observed, an attempt is usually made to reduce it. The general procedure for reducing an observed error is quite systematic, and is outlined below.

1. The specific method employed will depend upon the nature of the error. Consequently, the first step is an attempt to trace the error to a particular source or sources. Sometimes this tracing is an elaborate and systematic affair, and at other times certain sources of error are intuitively assumed. To find whether an error is random or determinate, or, if determinate, to find whether it is systematic, constant, or proportional, it is useful to study how the error varies with sample size and experimental conditions.

2. The most desirable method for reducing error is to select and con-

trol experimental conditions to reduce the error as much as possible. If, after this course has been followed to its practical limit, the error is not sufficiently reduced, further measures may be taken.

3. A random error may be decreased by increasing the number of determinations, but this is usually a last resort for chemical analyses, which are rather long and expensive. A predominantly determinate error may be allowed to occur under controlled conditions, and a correction may then be applied.

4. If it is not possible to discover the source of error, or if it appears that too much effort would be required to control the variables causing the error, the method of analysis may be rejected in favor of another. Often, when it appears that the search for the source of error and its elimination would be too difficult or long, other analytical methods are investigated without attempting to improve the method in question.

A specific illustration of this general procedure for reducing error is given in an investigation of the gravimetric determination of Al as Al_2O_3 (B8). In a first set of experiments the method as first devised was tested on known samples of potassium alum. The Al was precipitated with reagent-grade NH_3 as $\text{Al}(\text{OH})_3$, which was filtered, washed, ignited, and weighed as Al_2O_3 . Results are summarized in the first five columns of Table 5.1. The absolute error was fairly constant for sample sizes between 1 and 4 g of potassium alum, increasing only by about 30% for a fourfold (400%) increase in sample size. This error was found to be due predominantly to silica in the NH_3 , the silica being coprecipitated almost quantitatively with the $\text{Al}(\text{OH})_3$. Since the amount of NH_3 used was the same in all determinations, the error was constant. (The absence of positive error for the blank was explained by assuming that silica could not coprecipitate when there was no $\text{Al}(\text{OH})_3$ to carry it.)

TABLE 5.1

ERRORS IN THE GRAVIMETRIC DETERMINATION OF ALUMINUM AS Al_2O_3 *

SIZE OF ALUMINUM SAMPLE (g)	Al_2O_3 PRESENT (g)	Al_2O_3 FOUND, USING ORDINARY REAGENT-GRADE NH_3			Al_2O_3 FOUND, USING FRESHLY DISTILLED NH_3		
		Grams	Error		Grams	Error	
			Grams	Per Cent		Grams	Per Cent
1.0000.....	0.1077	0.1288	0.0211	16.4	0.1087	0.0010	0.9
2.0000.....	0.2154	0.2384	0.0230	9.7	0.2178	0.0024	1.0
3.0000.....	0.3231	0.3489	0.0258	7.4	0.3258	0.0027	0.8
4.0000.....	0.4308	0.4588	0.0280	6.1	0.4352	0.0044	1.0
Blank.....	0.0000	0.0000	0.0000	0.0000	0.0000	...

*Reprinted from A. A. Benedetti-Pichler, *Industrial and Engineering Chemistry, Analytical Edition*, 8, 373 (1936), Table 3, by permission of the publisher.

In a second set of experiments, summarized in the last three columns of Table 5.1, NH_3 was freshly redistilled and contained no silica. The error was greatly reduced, and the residual error was quite proportional to the amount of Al. This error was found to be due to retention of water, the amount of water retained being proportional to the weight of precipitate. The presence of this error is apparent in the first set of determinations, superimposed on the error due to silica.

It is conceivable that further experimental measures might be taken to reduce the error of water retention, but since it is so closely proportional to the weight of precipitate, a simple proportional correction of -0.9% applied to the weight of precipitate would reduce the over-all error to about 0.1% .

5E.2. Classification of Error According to Source

A classification of error according to source is useful in tracing an observed error, whether random or determinate. In chemical analyses there are three principal sources of error.

1. Errors due to the operator may arise from inexperience or carelessness. Typical of such errors, which are legion, are nonquantitative transfer of precipitates or samples, computational errors, improper sample preparation, and bias. For the novice such errors may range from small to large, but they should dwindle as experience is gained.

2. Errors may also be due to facilities, such as reagents, equipment, and the physical plant in which the operator works.

3. Errors inherent in the method of analysis are due to the nature of the reactions and substances involved. A few such sources of error are incomplete reaction or side reaction of a sought-for substance, solubility of a sought-for precipitate, or inadequate separation of interfering substances. For an acceptable method of analysis these errors must be kept below a certain limit, determined by the use to which the analytical result is to be put. This error, often called the "inherent error of the method," is usually given with the directions, and is the standard error expected of an experienced analyst working with good facilities.

It must be realized that errors due to the operator or to facilities may greatly aggravate the inherent errors of the method. For example, a method may be designed so that solubility losses are inappreciable provided that some precautions are taken. Failure on the part of the analyst to observe these precautions may lead to large errors. This disregard may take as simple a form as the use of indiscriminately large volumes of wash liquid for a precipitate that the analyst regards as "insoluble." For this reason it is important for the analyst to study in detail every method he undertakes, so that he may know the sources of potential error and guard against them.

5E.3. Methods of Reducing Determinate Error

The selection of experimental conditions to reduce a determinate error is the most desirable method, but this may be difficult, time consuming, or expensive. In such a case, another procedure is to allow the error to occur under controlled conditions, so that it may be as small and as reproducible as possible. With adequate control, a correction may then be applied to the result, or the determination may be carried out in such a way that the error is experimentally compensated for.

Several of the more popular methods for correcting or compensating for error in chemical analyses are outlined in the following sections.

5E.3a. Theoretical calculation of corrections. If a determinate error is ascribable largely to one cause, the magnitude of the error may sometimes be calculated theoretically, and a correction applied accordingly. The buoyancy correction in weighing is an example of the theoretical calculation of a correction. Loss in yield of a precipitate owing to solubility is sometimes calculated, though this is not a very accurate procedure. The change in concentration of a standard solution with change in temperature is often computed from the expansion coefficient of the solution. Usually, however, an error is due to several sources, and the theoretical calculation of the error and its correction is troublesome or inaccurate. In such cases it may be easier or more accurate to determine the magnitude of the error experimentally.

5E.3b. Calibration corrections. Direct calibration of weights or volumetric equipment is one of the simplest ways in which errors may be experimentally evaluated. The true weight or volume is found, from which a calibration correction characteristic of the piece of equipment is computed. The *calibration correction* represents the error of the piece of equipment, and is the quantity that must be added to the face value to give the true value.

5E.3c. Correction for constant error. The blank. If a determinate error is constant, reproducible, and independent of the amount of sought-for constituent, the magnitude of the error may be found by putting a known sample through the analysis. Thereafter this known, constant error is subtracted from each observed result to give the true value.

If the error is positive, it may easily be determined on a sample containing none of the sought-for constituent. Such a determination is called a *blank determination*, and the error is called the *blank*. If the error is negative, however, the blank determination is negative, and cannot be made; in this case the error must be determined on a sample containing a known amount of the sought-for substance.

As an example of the determination and use of the blank, suppose that an unknown sample requires 42.30 ml of standard solution for titration,

whereas a sample of distilled water containing none of the sought-for constituent requires 0.13 ml of standard solution. The blank is then 0.13 ml, and the corrected amount of standard solution required for titration of the unknown sample is $42.30 - 0.13 = 42.17$ ml. (The finite size of the blank may be due to impurities in the water or reagents used to prepare the sample.)

The treacherousness of applying a blank correction without full knowledge of the nature of the error is illustrated by the data of Table 5.1 (p. 47). Suppose that a worker runs a blank on a sample containing no Al, and finds it to be zero, as indicated in the table. If he erroneously concludes that the error is zero, and applies no correction in the analysis of finite-sized samples, his errors will be about 1% even if he uses redistilled ammonia, and 5–15% if he uses reagent-grade ammonia. The blank is also useless if the error is due to catalytic impurities in the sample or to an induced reaction. Park gives a systematic method of determining the blank and checking its constancy for varying sample size (P2).

5E.3d. Correction for proportional error. The control. If the determinate error is a proportional one, it may be compensated for by running a control determination—that is, by putting a sample with a known amount of the sought-for constituent through the analysis, and assuming that the result is proportional to the amount of sought-for constituent. The true amount of sought-for substance in an unknown sample is then found from the proportion

$$\frac{\text{Weight of constituent in unknown}}{\text{Weight of constituent in control}} = \frac{\text{result for unknown}}{\text{result for control}} \quad (5.10)$$

In this way proportional errors are cancelled, but constant ones are not. Whenever a proportional error is compensated for by running a control determination, conditions should be as similar as possible in both standardization and analysis, so that the same proportionality is maintained.

This procedure is employed in many cases where the reaction is non-stoichiometrical, that is, where the moles of reactant or product do not stand in a simple, whole-number relationship to the moles of sought-for substance.

In the gravimetric method (with redistilled NH_3) for the determination of Al, the proportional error due to retention of water may be reduced by taking the sample that contains 0.4308 g of Al_2O_3 as a control (Table 5.1). The weight of Al_2O_3 in any other sample may be computed by the use of Eq. 5.10. Thus the Al_2O_3 content of the sample giving 0.1087 g of precipitate is calculated as $0.1087 (0.4308/0.4352) = 0.1076$ g, which is only 0.1% below the true value of 0.1077 g. Applica-

tion of this method reduces the relative error due to retention of water from about 1% to only 0.1%.

Whenever a proportional error is small, it is proper and sometimes computationally simpler to apply a *proportional correction* instead of using Eq. 5.10. An example, also taken from the data of Table 5.1, is given on page 48.

5E.3e. Other methods of applying corrections. In practice, of course, a determinate error is seldom purely constant or purely proportional, but is usually a mixture of both. In such cases neither the simple blank nor the control determination may be used. However, more involved and troublesome compensation procedures do exist.

In one of these, the technique is identical with that of the control determination, with the added restriction that the sample size is chosen so as to contain about the same amount of sought-for constituent as the control (or vice versa). Then compensation for error is nearly perfect, no matter what kind of reproducible determinate error is involved. Compensation becomes less perfect as the difference increases between the size of the unknown and the control. In order to choose the appropriate sample size, a rough prior knowledge of the amount of sought-for substance is necessary. If this is not available, a guess must be made. If, as a result of a poor guess, there is a large difference between the unknown and the control, a second determination is performed that uses the result of the first to estimate the proper sample size.

In another correction procedure, the error is found as a function of sample size by running known samples of different sizes through the analysis. Corrections (i.e., those quantities that must be added to the observed results of the analysis to give the correct values) are then plotted as a function of the observed result, and a smooth curve is drawn through the points. For an unknown sample, the correction corresponding to any observed result may be found from this plot.

5E.3f. Limitations on the use of corrections. It is not always possible to reduce a determinate error to insignificance simply by applying corrections. Some limitations on the use of corrections are given in the Supplement (p. 636).

5F. ACCURACY SOUGHT IN CHEMICAL ANALYSIS

The accuracy sought in an experimental measurement is generally governed by the use to be made of the measurement. On the other hand, the accuracy achieved is determined by the method or facilities available.

In using a particular set of facilities and a particular method of measurement, there is a certain error inherent in any experimental result.

It is usually possible for the magnitude of this error to be reduced, but as the accuracy and precision are increased, longer and more refined methods and more elaborate facilities are required. A point is eventually reached where the increase in accuracy obtained is not worth the additional time, effort, and expense. In other words, speed and simplicity in measurement are not generally compatible with the highest accuracy.

In the light of this incompatibility, the accuracy that should be sought depends chiefly upon the use to be made of the result. This use determines the lowest accuracy acceptable. Only after this is known may an intelligent choice be made of the simplest, fastest, and least expensive method that will give this desired accuracy. Even though other more accurate methods or facilities may be available, these will not generally be used, since they are usually more complicated and expensive, and their higher accuracy is unnecessary.

The foregoing procedure for choice of the proper accuracy and method is the one that the professional chemist would follow. The student, however, has an entirely different objective, for he performs analyses primarily for the purpose of developing and testing his technique and knowledge. For this reason the student should seek to achieve the full degree of accuracy and precision inherent in the method. Only when the student can achieve such accuracy and precision has he mastered the knowledge and technique. With the equipment and techniques of elementary quantitative analysis, major constituents are frequently determinable within 1 p.p.t., and this is what the student should strive to attain.

As the proportion of sought-for constituent in a sample decreases below 10%, the attainment of a relative error as low as 1 p.p.t. becomes increasingly difficult. However, the accuracy required usually decreases as the proportion of sought-for substance decreases. For example, relative errors of 1 or 10% are often satisfactory in determination of substances constituting only 1 or 0.01% of the sample, respectively.

The random part of an over-all error can in principle be reduced by running a large number of determinations. In practice, this is not feasible, because chemical analyses are usually complicated, time consuming, and subject to determinate errors. If increased accuracy is necessary, other methods are employed. The number of determinations carried out by the analyst depends upon the purpose of the analysis. Usually one to four determinations are made.

An analysis is hardly ever based on one determination unless it is carried out by an accomplished analyst with proved methods and equipment. Even then, the result is still not trusted (because of the possibility of chance error) unless it is known beforehand approximately

what the result should be, as in routine testing, or unless the result is one in a series of values expected to show a certain trend. In other words, quantitative significance is seldom attached to one determination unless there is a check available from some other source.

To eliminate the possibility of large chance error, two determinations are frequently carried out by an analyst working with proved methods and equipment. If the two determinations do not check within the expected precision, or if one determination is spoiled before completion, additional determinations must be made.

Three determinations are frequently carried out by the beginner, so that there will still be two checking determinations left if one is spoiled in the run. Also, a much greater confidence may be placed in the result of three determinations than may be put in the result of two. (See the large jumps in s^2/σ^2 values and t values in passing from $N = 2$ to $N = 3$ in Tables S5.1 and S5.2, pp. 617, 622.)

Four or more determinations are not often performed in chemical analyses, unless they are simple or unless highly reliable results are desired.

5G. CHECKING THE ACCURACY OF ANALYTICAL PROCEDURES OR RESULTS

Even when a method is established, and workers and equipment are "beyond question," it is worth while occasionally to check results, to verify that facilities have not deteriorated or that incorrect practices have not crept in unsuspected. Also, if a new method of analysis is instituted, or if changes in procedure or equipment are made, or if an analyst tries a method for the first time, the accuracy of the results obtained should always be checked by one of the following methods: (1) use of another, independent, reliable method of analysis; (2) use of standard samples; (3) attainment of acceptable precision; (4) attainment of a material or ionic balance. Each of these commonly used methods is discussed in greater detail in the Supplement (p. 636).

These procedures are not all equivalent, nor do they all check the same sources of error. The one that should be used for a particular case depends upon the purpose of the check—that is, whether facilities, personnel, or the method itself are particularly suspect, or whether a whole procedure or just the analysis on a particular sample is to be checked. The time and effort available for the check and the reliability desired will also influence the choice. Study of these procedures reveals that no single one can give a certain check on the analytical accuracy of a particular sample or method. Thus it is desirable to check by more than one procedure, if great significance is to be attached to the check, and if time is available.

5H. COMPUTATION

5H.1. The Uncertainty of Experimental Quantities

Any experimentally measured quantity has inherent in it some error. Unless otherwise stated, the last digit written in such a number is assumed to be uncertain by ± 1 . Thus the length 1.013 cm does not mean exactly 1.013 cm, but rather that the value lies in the range 1.013 ± 0.001 cm, or 1.012–1.014 cm. The *uncertainty* of an experimental quantity may be expressed on an absolute basis. It may also be expressed relatively as the ratio of the magnitude of the uncertainty to the magnitude of the quantity itself. The absolute uncertainty of the foregoing length is 0.001 cm. The relative uncertainty is $0.001/1.013$, which may be expressed as 0.001, or 1 in 1000, or 0.1%, or 1 p.p.t. Table 5.2 contains self-explanatory examples. Note that the magnitude of the uncertainty itself is not expressed precisely.* Only its order of magnitude is important.

TABLE 5.2
THE UNCERTAINTY OF EXPERIMENTAL QUANTITIES

QUANTITY (CM)	UNCERTAINTY				NUMBER OF SIGNIFICANT DIGITS
	Absolute (cm)	Relative	Per Cent	Parts per Thousand	
1.11.....	0.01	1 in 100	1	10	3
0.11.....	0.01	1 in 10	10	100	2
0.111.....	0.001	1 in 100	1	10	3
0.011.....	0.001	1 in 10	10	100	2
2100.....	1	1 in 2000	0.05	0.5	4
2.1×10^3	0.1×10^3	1 in 20	5	50	2
0.0021.....	0.0001	1 in 20	5	50	2
0.002100.....	0.000001	1 in 2000	0.05	0.5	4
0.3720.....	0.0001	1 in 4000	0.03	0.3	4
0.003720.....	0.000001	1 in 4000	0.03	0.3	4
0.00372.....	0.00001	1 in 400	0.3	3	3

The order of magnitude of the uncertainty of a number may be expressed loosely by the number of *significant digits*. Any written digits that follow the first finite digit in a number are significant. Zeros preceding the first finite digit are not significant, and serve merely to locate the decimal point. Examples are given in Table 5.2.

*A number or a measurement with a low relative uncertainty (i.e., a large number of significant digits) is called "precise." Similarly, computations carried out to many digits are called "precise." This meaning of precision is decidedly different from its meaning when applied to describe the precision (scattering) of a set of measurements. It is pedagogically unfortunate that common usage has assigned two different meanings to the same term. Whenever the term is used, the student must decide from the context which meaning is appropriate.

There are mathematically defined quantities, such as integers, π , and e , that may be known to as many decimal places as desired, and that for all practical purposes possess no uncertainty. That is, they are always known with much greater certainty than the experimental quantities with which they are associated in computation. When such quantities are mingled with experimental ones, the student must decide from the context which quantities are experimental and which are defined.

Significant digits are not always used correctly. The age of the earth is frequently written as 4,600,000,000 years. This quantity is obviously not known to the nearest year, but as written there is no way of knowing the uncertainty exactly. Actually, the uncertainty is about 5%, and it is both more informative and more correct to write 4.6 billion years, or 4.6×10^9 years.

5H.2. Considerations in Computations

The precision of any computation should be commensurate with that of the data involved. If the precision of a calculation is much greater than that of its data, such computational precision is spurious, for the result cannot be more precise than the data from which it is obtained—a chain can be no stronger than its weakest link. On the other hand, if the precision of a calculation is much less than that of the data, considerable experimental pains that may have been necessary to obtain the precise data are wasted.

For example, suppose that the dimensions of a perfectly rectangular block are measured with a micrometer to be $1.003 \times 1.012 \times 1.008$ cm, with the purpose of calculating the volume. The first two of the following methods of computation are incorrect, and the third is correct.

Method 1. The computer reasons that each of the dimensions is very close to 1 cm, and that the volume is therefore $1 \times 1 \times 1 = 1$ cc. If the computation is carried out in such a way, the measurer might much more easily have used a centimeter rule instead of a micrometer.

Method 2. The computer multiplies the three dimensions as follows, retaining all (ten) digits in the product.

$$\begin{array}{r}
 1003 \\
 1008 \\
 \hline
 8024 \\
 1003\text{---} \\
 \hline
 1011024 \\
 1012 \\
 \hline
 2022048 \\
 1011024\text{---} \\
 \hline
 1011024\text{---} \\
 1023156288
 \end{array}$$

Method 3. In the computation shown in Method 2, the uncertain digits are italicized, both in the original dimensions and in the derived quantities. Thus every digit in the first product, 8204, is uncertain, because it is the product of 1003 by an uncertain number, 8, which could really be 7 or 9. Continuing this reasoning, every digit past the third in the result is uncertain, and to express the volume as 1.023156288 cc is unjustified. If the fourth digit is uncertain, then to retain any digits past the fourth is spurious and conveys a false impression of the precision of the result. The correct way to express the result is therefore 1.023 cc.

If this is realized, considerable effort may be saved in the calculation by rounding off the first product, 1.011024, to 1.011 before continuing. Although the saving is not great in this particular case, much effort may be saved when the computation involves multiplication or division of more than three factors.

It is not necessary to perform such a detailed analysis as the one above for every computation. Simple rules exist for computation that facilitate correct expression of the final result.

5H.3. Computation Rules

Rule 1. In expressing an experimental quantity, retain no digits beyond the first uncertain one.

Rule 2. In rounding numbers (i.e., in dropping superfluous digits):

- (a) Increase the last retained digit by one if the residue is larger than 5.
- (b) Retain the last digit unchanged if the residue is less than 5.
- (c) Retain the last digit unchanged if even, or increase it by one if odd, if the residue is exactly 5.

Example. When rounded to four digits, the numbers 1.02345, 1.02055, 1.02350, 1.02450 become, respectively, 1.023, 1.021, 1.024, 1.024.

Rule 3. In addition and subtraction, retain only as many decimal places in the result as there are in that component with the least number of decimal places.

Example.

21.1
2.035
6.12
<hr style="width: 100px; margin: 0;"/>
29.255 or 29.3

Rule 4. In multiplication and division, the answer should have a relative uncertainty that is of the same order as that of the least

precise component. The uncertainty of the answer should lie between one-fifth and twice that of the least precise component.

Example

(a) $21.1 \times 0.029 \times 83.2 = 50.91008$, or 51

↑
Uncertainty
is 1 in 30.

↑
Round answer so that its uncertainty
lies between twice 1 in 30 (i.e., 1 in
15) and one-fifth of 1 in 30 (i.e., 1
in 150).

(b) $173 \times 242 \times 891 = 37,302,606$, or 3.73×10^7

↑
1 in 200.

↑
Round answer so that its uncertainty
lies between 1 in 100 and 1 in 1000.

(c) $\frac{291 \times 272}{0.086} = 920,372$, or 9.2×10^5

↑
1 in 100.

↑
Round answer so that its uncertainty lies be-
tween 1 in 50 and 1 in 500.

In addition to the four fundamental rules above, there are a few others that sometimes prove helpful (see Supplement, p. 639).

5H.4. The Error of a Computed Result

The computation rules of the previous section are approximations, designed only to tell how many significant digits should be retained in a computed result. They are not sufficient for estimating the error of a computed result from the errors of the component factors. To estimate properly the error of a computed result, more refined mathematical methods must be used (see Supplement, p. 640).

A rough and frequently used concept is the maximum error of a computed result. The *maximum error* is an estimate of the error that is not likely to be exceeded in a small number of measurements. To obtain this, the maximum error of each component quantity is estimated, and it is then assumed that these component errors combine in such a way as to produce the maximum error in the result.

If there are many component quantities, the maximum error is overestimated, perhaps beyond all reason. This is dangerous, because it may lead to spurious experimental precision in an attempt to reduce this estimated error. Also, if the computation is not a simple one, the correct mode of combination of errors to produce a maximum effect on the result may not be apparent. The concept of the maximum error is used only by workers who are not familiar with σ and s as deviation measures, and it is at best only a nebulous way of expressing random error. It should not be used except in those cases involving simple computations with few component factors. In such simple cases, the pro-

cedure is satisfactory, and gives a rough estimate of an error that is seldom exceeded in practice.

Example. The maximum error of a reading on a buret is 0.01 ml. Measurement of a volume with this buret involves a difference of two readings. Since one reading could be high by 0.01 ml, and the other low, the maximum error in the volume measured could be 0.02 ml, and this could be either high or low. Usually, of course, the errors in the two readings would tend partially to cancel, so that the actual error in a measured volume could lie anywhere in the range from 0.02 ml high to 0.02 ml low.

QUESTIONS

Section 5A

- What is wrong or ambiguous about the following statements?
 - High precision implies high accuracy.
 - The accuracy of an observation is 0.3%.
 - "Deviation of the average" is synonymous with "average deviation."
 - The average weight is 7.1935 g.
 - The precision of a set of data is 0.5%.
- Why is the magnitude of the error of an experimental measurement seldom precisely known?

Sections 5B-D

- What is wrong with the following statements?
 - Any experimental error is either random or determinate.
 - In the absence of determinate error, the mean lies closer to the true value than any individual measurement does.
 - A mean of two determinations is less accurate than a mean of nine determinations.
- Classify the following sources of error as random or determinate, discussing the effect of each on the result of an analysis.
 - Solubility of the sought-for precipitate in a gravimetric analysis.
 - Arithmetical error resulting in an incorrect molecular weight of the sought-for precipitate in a gravimetric analysis.
 - Incomplete drying of the sample before portions are weighed out for triplicate analysis.
 - Incorrect concentration of the standard solution in a volumetric analysis.
 - Failure to judge the end point properly in a titration.
 - Indicator error in a titration procedure.
 - Loss of the sought-for precipitate during a transfer.
 - Incomplete ignition of a sought-for precipitate before weighing, giving a product of incorrect composition.
- Why is there so emphatic a distinction between μ and \bar{X} ? Between s and σ ? When could a measured \bar{X} be taken as equal to μ ? A measured value of s as equal to σ ?
- Rather than regarding systematic and constant determinate errors as being of two different kinds, it is more useful to regard them both as being constant determinate errors, with differing values of σ . Explain.
- Criticize the use of "determinate" in describing determinate error. Devise a better term and defend it.

Sections 5E-G

1. In an analysis where results are calculated using a control determination, why is it desirable to keep the unknown sample size similar to that of the control?
2. To be a basis for chemical analysis, must a reaction be stoichiometrical? What properties must the reaction have?
3. Why is it usually not very satisfactory to apply a correction for solubility losses?
4. Suppose that a -0.9% correction is applied to the determination of Al as Al_2O_3 , as suggested on page 48. List those conditions of the analysis that should be controlled as closely as possible in order to preserve the constancy of this correction.
5. It is decided to apply either a constant or a proportional correction to each of the following errors. Explain which would be best in each case.
 - (a) Error in weight of an object due to unequal lengths of balance arms.
 - (b) Change in concentration of a solution with temperature.
 - (c) Loss of AgCl owing to solubility in the gravimetric determination of chloride.
 - (d) Indicator error in a titration.
 - (e) Coprecipitation of impurities with the sought-for precipitate in a gravimetric analysis.
6. In standardizing a solution, why does an analyst seldom rely upon only one method of standardization? Under what conditions might the analyst rely upon only one method?

Section 5H

1. Define spurious computational precision, and give a specific example different from those already given in the text. Repeat for spurious experimental precision.
2. Three lengths are measured as 1.5, 3.1785, and 2.9 cm, with the objective of adding them together. What is wrong with this work?
3. Three dimensions are measured as 16.712, 0.031, and 9.564 cm, with the intention of multiplying them together. What is wrong with this work?
4. What is wrong with the following statements?
 - (a) The volume of a rectangular block measuring $1.1 \times 1.0 \times 0.9$ cm is 0.990 cc.
 - (b) The estimated cost of constructing a building is \$5,000,000.
5. In the illustrative example on page 57 (part a), are we entitled to say that the uncertainty of the answer is 1 in 51? Why?
6. In the expressions for the relative range or relative standard deviation (p. 40), it would be more correct to use the true value instead of \bar{X} , but the true value is not usually known. Explain why it is proper to use \bar{X} , making use of the data in the example on page 40.

PROBLEMS

Section 5A

1. Six measurements on the molarity of an HCl solution give 0.1502, 0.1508, 0.1497, 0.1509, 0.1484, 0.1506 M . Calculate \bar{X} . Also calculate \bar{x} , w , and s , in absolute and relative units. What is the error of \bar{X} , if the correct molarity is 0.1510 M ?
 Ans. $\bar{X} = 0.1501 M$;
 $\bar{x} = .0007 M$, 5 p.p.t.; $w = .0025 M$, 17 p.p.t.;
 $s = .0009 M$, 6 p.p.t.; error = $-.0009 M$, -6 p.p.t.
2. A sample of pure ZnO is analyzed to give the following percentages of Zn : 80.12, 80.07, 80.35, 80.17. Calculate \bar{X} . Give absolute and relative values for \bar{x} ,

s , and w . (Note that the units of absolute deviations are expressed as % Zn, whereas the relative deviations are pure numbers, expressed as per cent or p.p.t.) Calculate the error of the average.

3. For triplicate determinations on a copper sample, a student obtains 28.74, 28.78, 28.76% Cu. How should he report the result of his analysis?

Ans. 28.76% Cu; $N = 3$; $s = 0.02\%$ Cu.

4. Four determinations on the percentage of chloride in a sample give 0.35, 0.20, 0.30, 0.33. How should the results be reported?

Sections 5B-G

1. Five determinations on the molarity of an NaCl solution by a certain method under test give 0.2033, 0.2035, 0.2030, 0.2036, 0.2034 M . Five more determinations by another reliable method give 0.2030, 0.2028, 0.2029, 0.2026, 0.2027 M . For both methods, calculate the mean and the standard deviation. What is the error of the method? Speculate on the nature of the error.

Ans. Tested method: 0.2034 M , 1 p.p.t.;
correct method: 0.2028 M , 1 p.p.t.;
error, 3 p.p.t.; probably largely determinate.

2. The correct percentage of a sought-for constituent in a sample is 16.99%. Four determinations of this percentage by a method to be tested give 16.75, 16.89, 17.03, 16.93. Calculate the mean, standard deviation, and error of the method. Speculate on the nature of the error.

3. Eighty measurements on the Cu content in a sample give, in % Cu:

9.8	9.7	9.9	9.8	10.1	10.1	10.0	10.1
10.1	10.3	10.2	10.2	9.9	10.1	10.0	10.5
10.0	9.9	9.7	10.0	10.0	9.9	10.0	10.1
10.1	9.8	9.8	9.9	10.0	10.0	10.0	9.8
10.3	9.9	10.4	9.9	9.7	9.9	10.1	9.5
10.3	10.2	10.1	10.4	9.8	10.4	9.9	9.8
10.0	10.0	10.0	10.3	10.0	9.8	10.2	10.4
9.9	10.0	10.4	10.2	10.0	10.1	10.5	9.9
9.6	10.2	10.1	10.0	10.1	9.9	9.8	10.1
9.8	9.7	10.0	10.0	10.1	10.2	9.9	9.8

(a) Compute and tabulate the means for two randomly chosen groups of 4 measurements each, two groups of 10 measurements each, and two groups of 40 measurements each. Discuss the results.

(b) The correct percentage of Cu in the sample is 10.00%. Compute the errors of the six averages of part a. Do these errors decrease as the number of determinations constituting each set increases?

4. A volumetric method for the determination of chloride is tested on different-sized samples of pure NaCl, and the following results are obtained. Complete the following table and describe the nature of the error.

NaCl IN SAMPLE (g)		ERROR IN ANALYSIS	
Present	Found	Grams	Per Cent
None	0.0022		
0.1000	0.1023		
0.3927	0.3960		
0.8295	0.8311		
1.2976	1.3005		

5. In Prob. 4, the error may be decreased by applying a correction. (a) What is the best value to use as a blank? (b) Without regard for sign, what average residual

error is obtained through use of this blank? What is the nature of this residual error? (c) What minimum sample size should be used to keep the average residual error below 0.1%, using the blank correction?

Ans. (a) 0.0025 g;

(b) 0.0005 g, random; (c) 0.5 g.

6. In the determination of Zn with standard ferrocyanide, 0.319 g of pure ZnO requires 32.76 ml of standard ferrocyanide for titration. What is the % Zn in a 0.1763-g sample that requires 18.07 ml of the ferrocyanide solution? Assuming that the error is not completely proportional, what would be a better sample size to use?

7. In the Mohr titration for chloride with standard AgNO_3 , the blank corresponds to 0.18 ml of 0.1000 M AgNO_3 . How many grams of chloride are there in a sample that requires 48.71 ml of the AgNO_3 ? *Ans.* 0.1722 g.

8. In the Eschka method for determining S in coal, 1.000 g of coal, 1 g MgO , and 0.5 g Na_2CO_3 are used. The weight of BaSO_4 obtained is 0.1532 g. A blank analysis on 10 g MgO and 5 g Na_2CO_3 gives 0.0897 g BaSO_4 . What is the % S in the coal?

9. A gravimetric method for Ca consists of precipitation and isolation of the oxalate, ignition to CaO , and weighing of the CaO . Analysis of samples of pure calcite (CaCO_3) containing known amounts of Ca gives the following results. Complete the table and state the nature of the error.

Ca IN SAMPLE (AS g CaO)		ERROR	
Present	Found	Grams	Per Cent
None	None		
0.1000	0.1005		
0.2530	0.2540		
0.3972	0.3996		
0.5296	0.5328		
0.8325	0.8356		
1.0596	1.0639		

10. In Prob. 9, calculate the best correction to apply to the method, and estimate the average residual error (without regard for sign) after applying the correction.

Section 5H

1. Specify the absolute and relative uncertainties of the following experimentally measured lengths, in centimeters. Also, give the number of significant digits in each length. (a) 672.25, (b) 6.7225, (c) 0.0004, (d) 0.0004000, (e) 0.02136, (f) 4.0×10^{-4} , (g) 4.0×10^4 .

Ans. (a) 0.01 cm, 1 in 70,000, 5;

(d) 10^{-7} cm, 1 in 4,000, 4;

(g) 0.1×10^4 cm, 1 in 40, 2.

2. Rule 4 for multiplication and division is sometimes erroneously stated: "The number of significant figures in the result must be the same as the number of significant figures in the least precise component." Show how this rule is invalid for the following cases, which occur quite frequently: (a) 0.9×1.4 . (b) 8.13×1.2661 .

3. Express the results of the following computations:

(a) $2.2931 + 6.0 - 7.12$

(f) $0.8743 + 3.5 \times 10^{-4} - 0.0008743$

(b) $2.13 + 1.9038$

(g) $(1.8763 + 2.0)10^{-4} + .000897$

(c) $2.03/1.00735$

(h) $\pi \times 63.41 \times 1.7983 \times 10^{-8}$

(d) $8.26 \times 1.23456 \times 10.83$

(i) $(0.372 + 0.002)10^6 \times 22.7$

(e) $87.41 \times 2.0/2.013$

(j) $(0.202 + 0.020)^2 \times 18.6$

Ans. (a) 1.2; (e) 87; (j) 0.917.

4. The weight of a 0.4-g sample is to be obtained with a maximum error of 0.1%. Within what error must each weighing be made if the weight of the sample is obtained

as a difference in weight between an empty container weighing 30 g and the container filled with the sample?

5. There are 96,496 coulombs per equivalent. How many coulombs are there in 0.00119 equivalent? *Ans.* 115 coulombs.

6. A buret reading may be made with a maximum error of 0.02 ml.

(a) What is the maximum error in a measured volume of 30.00 ml?

(b) What would be the maximum discrepancy between two such measurements on the same volume?

(c) In order that the volume be known with a maximum error of only 0.1%, what should be the smallest volume measured?

7. A sample requires 40 ml of a standard solution for titration. A blank correction of 0.15 ml must be applied. What are the absolute and relative errors allowable in the blank, so that the error of the blank causes an error of less than 0.1% in the total volume? *Ans.* 0.04 ml, 30%.

6 INTRODUCTION TO LABORATORY WORK

Sensible orientation is helpful in beginning the study of any subject, and it is particularly necessary for quantitative analysis. The student must learn the objectives of study early. If necessary, he must review mathematics and elementary chemistry. And in the laboratory he must master a minimum number of techniques as soon as possible. In order to reduce wasted effort, the first few periods of laboratory work should be outlined rather carefully by the instructor, and the organization of the laboratory course should be described. After this, the student is expected to plan his own work, with decreasing help from the instructor.

Since the organization and objectives of the analytical course are so highly dependent upon the individual instructor and upon the facilities available, it may be necessary to supplement these introductory instructions with others that are more appropriate. Where such modified or additional instructions are used, the student must realize that they take precedence over the ones in this chapter.

6A. BEGINNING LABORATORY WORK

During the first laboratory period, the student should:

1. Obtain locker, balance, and weight assignments.
2. Check his locker contents against Appendix III (p. 910) or against the list provided. Note in particular that buret and pipet tips are not chipped, and that glass or porcelain ware is not cracked. Any defective apparatus should be replaced. This must be done during the first labora-

tory period, since charges are made for equipment withdrawn from the stock room thereafter.

3. Construct the following apparatus (p. 134): 9 stirring rods, 9 glass hooks, 4 droppers, 1 right-angle bend, and 2 wash bottles (500 ml and 1 l). If some of these items are already in the locker, it will be necessary only to repair the existing items, or to construct additional ones to fill out the list. If this work is not completed by the end of the first laboratory period, it should be finished during free moments in the future, and not at the beginning of the second laboratory period, which would delay the start of the first experiments.

4. Clean the desiccator, and add fresh anhydrous CaCl_2 (p. 108).

5. Prepare 200 ml of cleaning solution (p. 248).

6. Learn the location, functions, and use of the community equipment, such as balance room, stock room, drying ovens, muffle furnaces, fume hoods, sand bath or hot chest, bulletin boards, first-aid cabinet, etc. It is extremely important that this apparatus be used properly and with consideration for one's fellow students; improper use of these facilities by just a few people may cause great inconvenience for the whole class (p. 139).

6B. PERFORMING LABORATORY WORK

The laboratory work consists largely of the analysis of unknown samples. Each student should obtain a list of the required determinations. If possible, he should schedule these determinations, and should make a conscientious effort to remain approximately abreast of this schedule throughout the semester.

Procedures for reporting and grading analyses and for withdrawing unknowns will be determined and explained by the instructor.

Analytical techniques are described in chapters 8 (gravimetric) and 15 (volumetric). The student should scan these chapters early, simply to become familiar with the contents. Then when the need for a certain technique arises in a particular determination the appropriate parts of these chapters should be critically studied.

6B.1. Suggestions for Work

In making suggestions for the study and practice of analytical chemistry, it is difficult for the instructor to avoid exhortation. To the student, some of the suggestions made by the instructor at the beginning of the term may seem fussy, arbitrary, and unnecessary. To prevent the formation of such an (erroneous) opinion, the student should scan some of the experiments for an idea of the sort of work he will be ex-

pected to perform. Only after the nature of the experimental and theoretical work has been fully understood will the suggestions of the instructor take on their full significance. If they are ignored, considerable damage may occur to both the student's attitude and his working habits. It is hoped, therefore, that the habits and qualities outlined below will be developed; time and experience will demonstrate their correctness.

Cleanliness. Desk, balance, and locker should be kept uncluttered and in constant order. There should be no need to clean up extensively at the end of the laboratory period. It is much easier to clean glassware as one works than after it has become encrusted and dusty. Equipment should be clean on the outside as well as inside, if for no other reason than that it is difficult to tell if the inside is clean when the outside is dirty.

Care. Carelessness spoils not only one's own work, but often that of others also. In the laboratory, where so much equipment is used jointly, care, consideration, and practice of the Golden Rule become mandatory if undeserved misfortune is to be avoided. A distinction should be drawn between carefulness and fussiness, for the latter reduces speed and efficiency.

Judgment. The student should learn to exercise good judgment. At the start, this ability is limited because of lack of experience. There are many occasions where judgment must be used. Each time an error is made, judgment is required to decide whether the error is significant or insignificant, or rectifiable or unrectifiable. The student should try to make himself independent of his instructor's assistance as soon as possible.

Dexterity. None of the operations of analytical chemistry are really difficult, but they do require some nimbleness. Practice on some of these operations before they are put to use on unknown samples will help to prevent accidents and spoiled determinations.

Planning. Laboratory work should be planned and scheduled very carefully before performance. There are steps in some determinations that must be carried out without interruption; planning is necessary to accommodate these. Also, some operations may require only a small proportion of one's attention, or they may involve waiting periods. Planning is necessary to fill these intervals with other work, or to adjust the schedule so that these periods will fall between laboratory sessions. It is advantageous to overlap experiments so as to avoid idle periods.

Proper planning involves the reading and study of the whole procedure, from beginning to end, before any work is undertaken. Special attention should be given to possible sources of error and ways of avoiding them. After such study, a summary data page should be drawn up in the notebook and a working outline should be prepared. Only then

should laboratory work be initiated. Failure to plan in this way inevitably leads to mistakes, loss of time, and poor understanding of the subject. The student who occupies his hand, mind, and eyes by holding a textbook constantly between himself and his work cannot possibly give proper attention to his work.

Speed and efficiency. Speed, although desirable, should never take precedence over care and thoroughness. At the beginning of the term the student should not strive too hard for speed, for there are many other more important habits to acquire. After some experience and dexterity are obtained, greater attention may be paid to working rapidly. Efficiency comes almost automatically if planning and organization are carried out properly.

Accuracy. It is usually necessary for the student to revise his ideas of accuracy in beginning his study of quantitative analysis, since the goal aimed at is probably considerably higher than that previously attempted. The concepts of accuracy, precision, and spuriousness should be learned early.

Constructive criticism. The student should be critical, but constructively so. For example, the correctness of a weight set or the purity of a reagent should never be taken for granted if it is possible to test it without great effort.

Honesty. The student should be honest and unbiased in recording and interpreting data. Complete impartiality is surprisingly hard to acquire, and constant effort is required to avoid bias. Many factors operate constantly to prejudice the laboratory worker, and if he yields to these there is a high probability that his work will suffer. Everyone occasionally has to fight the tendency to bring duplicate determinations closer together by some arbitrary means, or to alter a result to bring it closer to a preconceived value, or to go on with a determination after an error has been made, and then to accept it if it agrees with another determination. Such practices are fruitless, pointless, and erroneous; but it is difficult to prove this, because by chance they "pay off" once in a while. It is sometimes difficult for the student to see that the "odds" are really against him in the long run if he yields to such bias.

Correlation. Experiments should be studied not only before performance, for proper planning, but also afterward, for correlation of theory and practice in the light of what was observed during performance.

Cooperation. Cooperation with one's classmates and the instructor is highly desirable. Balance partners, particularly, should work as a team rather than as individuals, in order to prevent conflict and delay.

Safety. In connection with certain techniques and operations described in this text, safe practices are also described. However, a chemical laboratory is filled with hazards, and working safely demands

more than the negative attitude of not doing certain things. Safety demands common sense, care, and a positive willingness to take precautions even though one can usually "get away" with not taking them. Thus, safety glasses should always be worn in the laboratory. Of what benefit is it to a student who has splashed acid into his unguarded eyes, if he has previously gotten away a thousand times without the use of safety glasses?

Another cause of many accidents is haste, which is usually a consequence of poor planning. In the laboratory, haste should be avoided like the plague; it is much better to finish less work carefully and properly than it is to finish more work carelessly and dangerously. In the long run, the time "saved" by careless haste is lost in accidents.

6B.2. The Laboratory Notebook

The laboratory notebook is of great importance, for it is the medium through which the worker's results are preserved and transmitted to others. Experimental work is wasted if it is inadequately reported. One *criterion of the quality* of a notebook is that a person desiring to know the result of an analysis should be able to find it in the notebook with a minimum of effort, without having to read or search through much extraneous material. He should also be able to obtain detailed information easily on any part of the analysis in question. If this can be done, the notebook is a good one; if not, it is poor.

There is a penalty for recording data incompletely, and for transmitting it inefficiently to another interested person. The student may discover this when he finds the instructor unable to help him trace errors or to choose among discordant results, or when work must be repeated simply because conclusions cannot be drawn from the poor record.

The notebook itself should be bound and adequately large (8 by 10 inches). Data, observations, and conclusions should be recorded in ink in this book only—never on loose sheets of paper. The record should be maintained as the experiment progresses; reliance upon memory for any appreciable length of time is poor practice. Erroneous work should never be crossed out so completely as to be illegible, nor should pages be removed. Instead, data may be rejected by a single line drawn through them or by appropriate annotation. This is very important, for examination of such work later often leads to useful conclusions, and sometimes establishes the correctness of the rejected data.

Everything possible should be done to *classify the information* in the notebook. All pages should be numbered. Several pages should be reserved at the beginning of the book for a table of contents. As the work proceeds, the title of each experiment and the number of its summary data page should be added to the table.

The contents of each experiment should be summarized. A *summary data page* should be prepared before the experiment is performed, and should contain space for the significant data to be filled in as the experiment progresses. The results of the analysis, as calculated from these data, should also be given on this page. Most of the information on this summary data page is obtained from original data that may have been recorded elsewhere in the notebook. Page numbers that locate these original data and any associated computations should be indicated along with the information entered on the summary page. For example, the weight of a crucible plus sample may be entered on the summary page. This weight may be derived from a whole page of balance swings, rest points, and calculations. The number of this page should be indicated with the weight on the summary page, so that the original data may be easily found and checked, if necessary. Specific examples of summary data pages are given for a few key experiments in the text (pp. 157, 216, 294).

Each page should have a brief title, so that its contents may be known at a glance. It is also important that each piece of work be dated.

The notebook should contain a thorough record of observations made during the work. Under no circumstances should there be a verbatim transcription of directions from the text. Instead, a working outline of each day's work should be prepared in advance. The student should have the experiment well enough in mind so that he may work from this outline, with only occasional reference to his textbook.

6B.3. Details of an Analysis

The determination of a substance is usually a detailed process that is highly dependent upon the particular properties of the sought-for and interfering substances. For each experiment described in this text, the working procedure is given as briefly as possible. Details supporting the working procedure are gathered as notes following the procedure. Much of the information in these notes is of importance only for the particular determination at hand; it is often not of great general importance. However, these details are typical of the information which should be obtained and studied before the actual performance of any determination. If an analysis is undertaken without proper attention to such details, the chances of error become great.

6C. TERMINATING LABORATORY WORK

The last laboratory period of the semester is reserved for checking out of the laboratory. No experimental work may be performed in this

period; all reports are due at the beginning of the last laboratory period, and none is accepted later without a valid excuse and the consent of the instructor. All students must be checked out by the end of the last laboratory period. The procedure for checking out is as follows:

1. Check locker contents against the lists in Appendix III (p. 910) or against the list provided. Replace any missing or damaged pieces. Clean, rinse, and drain all glassware. Crucibles must not be etched or cracked. Pipets and burets must not be chipped. Rubber tubing and policemen should be disconnected from apparatus and glassware. All excess and community equipment should be returned to the stock room or to the proper place in the laboratory. A moderate amount of breakage is allowed, but the student is billed for excessive breakage at the end of the semester.

2. Empty all reagent bottles into the sink, rinse them with distilled water, and drain them. Before storing away, put strips of paper in the necks of all glass-stoppered bottles to prevent the stoppers from sticking.

3. Remove the desiccant from the desiccator (unless otherwise directed), clean all grease from rim and cover, and store with cover turned upside down on the desiccator.

4. Line locker drawers and shelves with clean paper.

5. Each balance should be checked cooperatively by the students using it, and any maladjustment reported to the instructor. The rest point should be within 0.5 division of scale center, the sensitivity should be 2–4 div/mg, and the pans, platform, and case should be clean. The weight set should be complete and clean.

6. When the foregoing work is completed, secure the instructor's approval for checking out.

7 THE ANALYTICAL BALANCE

Almost every chemical analysis requires the accurate weighing of samples. Use of the analytical balance is therefore the first step to be learned, for no elementary analysis may be undertaken without it.

7A. THEORY AND CONSTRUCTION

7A.1. Principles of the Balance

The balance may be thought of as a weightless, equal-arm, first-class lever, balanced at the center. An object to be weighed is suspended from one end of the lever, and known weights are added to the other end until the lever assumes a horizontal position. At this position, the mass of the object must be equal to that of the known weights. The balance is simply an instrument for comparing two masses, which indicates when the unknown mass of the object becomes balanced by an equal amount of precisely adjustable and known mass. (The distinction between mass and weight is given in the Supplement, p. 649, but is not important for elementary balance theory.)

The picture above is an ideal simplification. In practice, a weighing could not be made with a weightless beam balance, because the masses could never be adjusted exactly enough to balance the beam; the slightest inequality between the object and the weights would cause the beam to tilt, and the tilting would not cease until the beam assumed a vertical position.

To be practical, a balance beam must have mass, which may be considered concentrated at the center of gravity (c.g.). For a stable bal-

ance, the c.g. must be below the fulcrum. Figure 7.1 shows the important parts of a practical balance. If the beam-pointer system is symmetrical about the vertical plane through the fulcrum, the c.g. lies vertically below the fulcrum at equilibrium, and the pointer rests at the center of the scale. If a slight increment of mass is added to one pan, the beam begins to tilt. In tilting, the c.g. begins to move out of the vertical plane through the fulcrum, and begins to exert a restoring torque. This restoring torque increases with the angle of tilt, and eventually balances the moment due to the weight increment. At this point the tilting stops, and the beam assumes equilibrium in a tilted position.

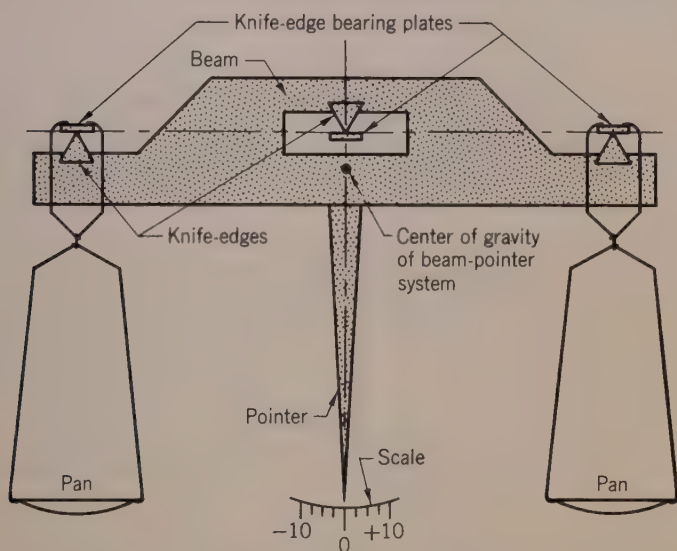


FIG. 7.1. Important Parts of a Practical Balance

7A.2. Sensitivity of the Balance

It may be shown that the angle of tilt and the distance over which the pointer moves on the scale are proportional to the mass difference between the object and the weights (see Supplement, p. 650). Thus

$$\left(\begin{array}{l} \text{Displacement of pointer} \\ \text{in scale divisions from} \\ \text{unloaded rest position} \end{array} \right) = k \left(\begin{array}{l} \text{mass difference} \\ \text{between object} \\ \text{and weights} \end{array} \right) \quad (7.1)$$

The proportionality constant, k , is called the *sensitivity* of the balance, and is defined as the displacement of the pointer in scale divisions produced by a change of 1 mg in the load on either pan.

$$k = \text{sensitivity} = \text{divisions per milligram} \quad (7.2)$$

The sensitivity is an important quantity, since it not only characterizes the balance, but is also used in weighing calculations.

It may be shown theoretically (see Supplement, p. 652) that the sensitivity is directly proportional to the lengths of the pointer (R) and balance arm (L). The sensitivity is inversely proportional to the dis-

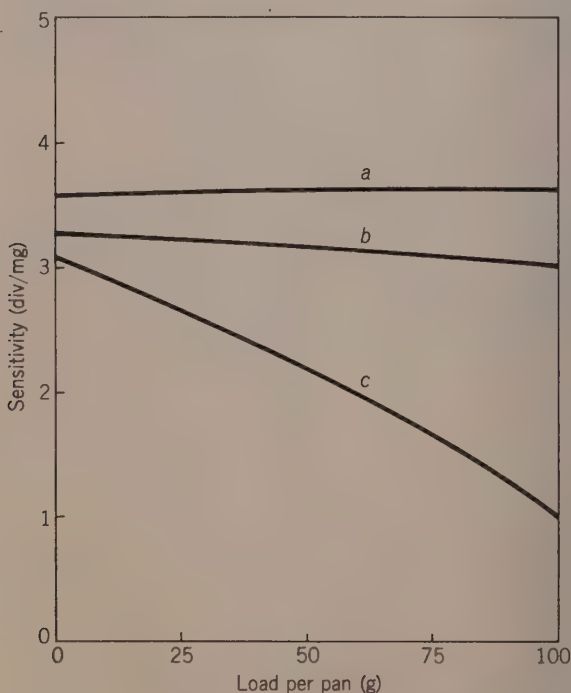


FIG. 7.2. Dependence of Balance Sensitivity upon Load

tance (r) of the c.g. from the fulcrum, and to the mass (M) concentrated at the c.g. (These relationships should be verified qualitatively by considering the mode of action of the balance.)

Sensitivity is also dependent upon the load in the pans. (This dependence is critically discussed in the Supplement, p. 652.) Typical load-sensitivity curves are given for different kinds of balances in Fig. 7.2. Curves between a and b are characteristic of good balances, whereas worn balances exhibit curves like c . Because of the variation of sensitivity with load, the sensitivity is always determined at the particular load being weighed.

7A.3. Balance Design

It might seem that balances should be designed for maximum sensitivity. However, attempts to increase sensitivity are accompanied by disadvantages.

1. It is not possible to change some of the sensitivity-determining factors (R , L , M , and r , above) without adversely affecting others. For example, an increase in the balance-arm length requires more material and increases the mass of the beam. This decreases sensitivity.

2. As the sensitivity increases, the balance becomes more inconvenient to use. The tolerable weight difference between the object and the weights that still allows the pointer to swing on scale decreases, and more painstaking counterbalancing is therefore required in the weighing process.

3. As sensitivity increases, the stability decreases; that is, the balance becomes more subject to disturbances such as vibration, air currents, and frictional effects. A limit is eventually reached where a further increase of sensitivity is offset by a decrease in stability.

4. As sensitivity increases, the period of the balance increases (see Supplement, p. 653). Longer times are then required for weighing.

No one of these characteristics may be emphasized to the disadvantage of the others, and balance design requires a careful and artful compromise among all of them.

7A.4. Balance Construction

The ordinary analytical balance is capable of weighing objects up to 100 g with a precision of 0.05 mg, or 1 part in 2 million. In addition, a good balance must be convenient to use and must have stability, sensitivity, and a fairly short period. The construction of balances that meet all these requirements is no mean feat of engineering. A good balance is one of the finest and simplest instruments at the disposal of the chemist. It deserves every consideration in care and use.

In addition to the essential parts of Fig. 7.1, a real balance has a number of extra features that are necessary for efficient weighing; they are shown in Fig. 7.3.

The heart of the balance is the beam, B , with a central knife-edge, E , and two pan knife-edges, D , set at the ends of the beam. All three knife-edges are pressed permanently into the beam, with the central one pointing downward and the end ones pointing upward. For lightness and maximum sensitivity, the beams of most modern balances are invariably made from an aluminum alloy. The construction is trussed, rather than solid, with large parts cut away so that it may be light in weight, yet rigid. For the balance to be stable and unchanging with

age, the beam and all other parts must be properly finished. All surfaces must be treated to reduce corrosion, and careful machining is essential to avoid strains that might require years to disappear (A3). The materials that comprise the beam-pan system must be very carefully

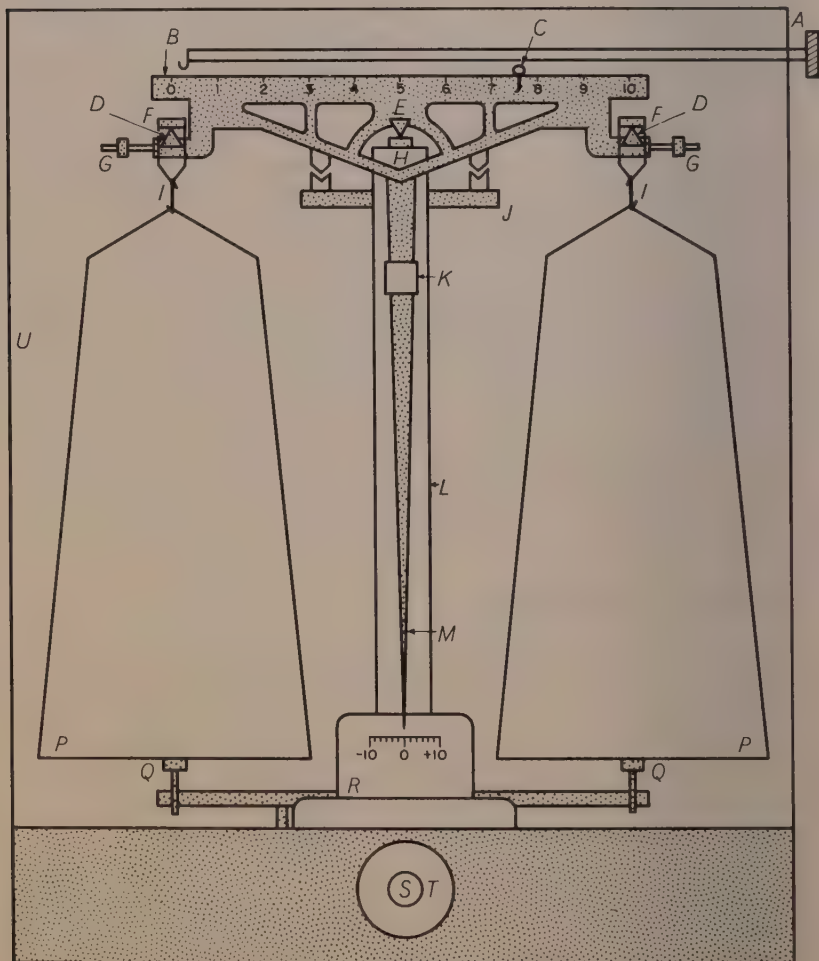


FIG. 7.3. Parts of the Ordinary Analytical Balance

chosen. Lacquers are no longer used for finishing, and cements are held to a minimum, to avoid hygroscopicity that would cause the rest point to shift with relative humidity (A6).

Knife-edges are made from agate, because of its hardness and resistance to corrosion. Agate, however, is also brittle, and great care must

be used to prevent chipping due to shock. The central knife-edge rests on an agate plate, *H*, set on the post, *L*. The pan knife-edges bear on agate plates, *F*, which are set in stirrups, *I*, which in turn support the pans, *P*. Each stirrup ends in a double hook; the upper holds the pan and the lower is for the suspension of objects that cannot be set securely upon the pan.

When not in use, the beam is arrested with a quarter turn clockwise of the large knob, *T*. This raises the support bar, *J*, which raises the beam so that the knife-edge, *E*, is free of its bearing plate. The pan knife-edges are also raised from their bearing plates by this operation, though this is not apparent from Fig. 7.3, which omits this detail for simplicity. There are many other types of arresting mechanisms, all of which must act gently and precisely to minimize wear on the knife-edges.

The pan arrests, *Q*, are activated by a small push button, *S*, which is concentric with the beam arrest knob, *T*. Pushing this button in and turning a quarter turn counterclockwise locks the pan arrests in the depressed position, so that the pans may move freely. When the button, *S*, is out, the pan arrests push lightly against the bottoms of the pans. On some of the older models, the pan arrest knob is located apart from the beam arrest knob.

It is not possible to manufacture pans that are exactly equal in weight. The small nuts, *G*, are adjusted at the ends of the beam so that the rest point at zero load is at the scale center.

The balance point is indicated by the pointer, *M*, which swings over the scale, *R*. The small brass collar, *K*, is movable along the pointer, and is used to adjust the sensitivity of the balance. The whole assembly is covered by a protective glass case, *U*, to keep out drafts, dust, and corrosive fumes. The rider, *C*, is adjusted from the outside of the case with the rider control, *A*.

Lewin describes the construction and compares characteristics for many of the commercially available balances (L9).

7B. WEIGHTS

The weights in a set consist of two kinds. The *integral weights* are of the following denominations: 50, 20, 10, 10', 5, 2, 2', and 1 g. The *fractional weights* are: 500, 200, 100, 100', 50, 20, 10, and 10' mg. Weights from 0 to 10 mg are added by placing the rider, *C* (Fig. 7.3), at different positions on the graduated beam. Where there are two weights of the same value in a set, one is dotted to distinguish it from the other for calibration purposes. Some newer sets of weights have

the sequence 5, 3, 2, 1 in both integrals and fractionals, so that no two weights in a set are alike.

Weights, of course, are never exact, but are constructed within certain tolerances. The National Bureau of Standards specifies many different classes of weights, each of different accuracy. Construction and tolerance limits for the classes sufficiently accurate for analytical chemistry are given in the Supplement (p. 653). A set of weights should never be assumed correct until it is checked.

7C. DIRECT WEIGHING PROCEDURES

Two complications keep the weighing process from being a very simple one. (1) The pointer never comes to rest, and the rest point must be estimated. (2) It is troublesome and time consuming to achieve an exact counterbalance between the object and the weights. This section describes several weighing procedures that differ not in principle, but only in the way in which these complications are met.

The method of long swings should be learned first, since it illustrates weighing principles most effectively. It is also the most precise of the procedures described in this book, and is most frequently used with microbalances. After some feeling for the balance is acquired, it is advisable to shift to the faster short-swing method, which is the most suitable for ordinary quantitative analysis. The very rapid single-swing method is described in the Supplement (p. 656).

7C.1. Method of Long Swings


The four steps in the method of long swings are outlined below, with an example and with suggestions on weighing procedure.

Obtain the zero rest point. With both pans empty, the zero rest point (0-r.p.) is obtained as follows. The balance case should be closed and the rider set on zero. Before the beam is released, the pan arrests are momentarily pushed in and released several times. This is done to center the pans, so that they will not oscillate independently about their knife-edges and impart irregularity to the pointer swings. The beam is lowered onto its knife-edge with the beam arrest, and then the pan arrests are lowered so that the balance is free. If the pointer swing does not cover five to ten divisions on the scale, an impulse may be given to the beam by momentarily placing the rider in an off-balance position. (Do not fan the air or touch the pans to start oscillation; these techniques lack control.) For a steady state to be reached, the first few swings are allowed to go by before readings are taken.

The 0-r.p. is determined by recording an odd number of consecutive

pointer swings, the scale being read to the nearest tenth of a small division. The $-10, 0, +10$ scale-numbering system should be used, the center division being taken as zero. Readings to the left of zero are negative, and readings to the right are positive. Three swings are recorded for ordinary work, and five for more exact work. To estimate the 0-r.p. (a) average the odd number of readings on one side, and (b) average the even number of readings on the other side. (c) The 0-r.p. is the average of the two averages. (For the theory of estimating the r.p. of a damped oscillation, see the Supplement, p. 655.)

As an example, suppose that the swings for a balance with both pans empty are as given below. The 0-r.p. is calculated as shown.

-4.2		+3.0	
-4.0		+2.8	-4.0
-3.9			+2.9
$3 \overline{) -12.1}$		$2 \overline{) +5.8}$	$2 \overline{) -1.1}$
-4.0		+2.9	-0.6 0-r.p.

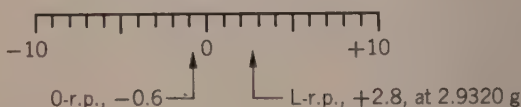
To arrest the balance, the pan arrests are released as the pointer passes through the scale center, and then the beam is raised. The beam should not be raised or lowered unless the pans are arrested.

Obtain the approximate weight of the object. With the balance arrested, the object to be weighed is placed in the center of the left-hand pan. Weights are added to the right-hand pan, starting with a weight thought to be slightly heavier than the object, and working down to the smallest fractional. After the addition of each weight, the beam is very gently lowered only part way, and the direction of the pointer deflection is then noted in order to determine the inequality between weights and object. If there is a deflection of the pointer, the inequality between the object and weights is greater than 2 g, which is the maximum difference supportable by the pan arrests alone. If there is no deflection on lowering the beam partly, it should be lowered all the way, and then the pan arrest should be momentarily depressed. The deflection of the pointer reveals whether the weights are lighter or heavier than the object. If the weights are heavier than the object, the smallest weight on the pan is removed and replaced with the next smaller one from the box. If the weights are lighter than the object, the next lower weight in the box is added to the pan. This procedure is followed until the smallest weight in the set has been tried. The balance should always be arrested when articles are added to or taken from the pans. In adding weights, the heavier one should be placed toward the center of the pan, and the

lighter ones evenly distributed around them, so that the pan hangs vertically.

When this first, rough counterbalance is reached, the balance case is closed and the rider is adjusted so that the pointer swings on the scale when the balance is freed. The load rest point (L-r.p.) is then taken, and the sum of the weights in the pan plus rider is recorded as the approximate weight of the object. This weight is only approximate, because time is not taken to adjust the L-r.p. to the 0-r.p. Before the sum of the weights in the pan is recorded, this sum should always be checked by adding the vacancies in the box. It is desirable to record individual weights, unless the set is known to be error-free or unless the weights are used in a very systematic manner.

Continuing with the example started above, suppose that the L-r.p. is $+2.8$, with the object in the left pan counterbalanced by 2.9320 g in the right pan, including the rider at 2.0 mg .



The difference between the 0-r.p. (-0.6) and the L-r.p. ($+2.8$) indicates that the weights are lighter than the load. To obtain the exact weight of the object, the weight corresponding to $+2.8 - (-0.6) = 3.4$ divisions must be added to the approximate weight (2.9320 g). Before this weight can be calculated, the sensitivity must be known.

Obtain the sensitivity. The sensitivity is obtained at the load in question by moving the rider 1 mg either way on the beam and noting the change in rest point.

Continuing with the example above, suppose that when the rider is moved to the 3.0-mg position, the r.p. becomes -0.8 . The 1-mg change therefore changes the r.p. from $+2.8$ to -0.8 , or 3.6 divisions. The sensitivity is therefore 3.6 div/mg .

If a load-sensitivity curve is available, the sensitivity at the load in question may be found from the curve and the experimental determination may be omitted. Because the sensitivity is dependent upon so many factors, however, it is necessary to check the sensitivity curve very frequently to make certain that it has not changed.

Calculate the exact weight. The exact weight of the object may be calculated from the data of steps 2 and 3 above. The difference in milligrams between the object and the weights is calculated and applied to the approximate weight to give the exact weight.

Concluding the example above, the difference between the object and the weights is $3.4\text{ divisions} = 3.4/3.6\text{ mg} = 0.9\text{ mg}$. As shown in step 2,

this difference in weight must be added to the approximate weight (2.9320 g) to give the exact weight of the object, which is therefore 2.9329 g.

7C.2. Method of Short Swings

The rider is adjusted until the L-r.p. agrees with the 0-r.p. within 0.1 mg, and then the weight of the object is taken as equal to the known weights. How close the two rest points must be for agreement within 0.1 mg depends upon the sensitivity. Since all balances should have sensitivities of at least 2 div/mg, two rest points lying within 0.2 division of each other may be considered identical. In adjusting the rider, it is helpful to know the approximate sensitivity.

When the rider is thus precisely adjusted, the L-r.p. falls close to the scale center. If the balance is carefully freed, the swings are short, say, 2–3 divisions. Damping is then small, and the r.p. may be estimated mentally as the average of two consecutive pointer readings.

As an example of this procedure, suppose that a balance has a 0-r.p. at -0.5 division, and that the sensitivity is about 4 div/mg. The object is placed in the left pan, weights are added to the right pan in the usual manner (say, 10.350 g), and the rider is given a first setting on 8.9 mg, so that pointer readings are $+2.0$, -1.0 . The L-r.p. is then $(+2.0 - 1.0)/2 = +0.5$ division. This is 1.0 division to the right of the 0-r.p., which means that the weights are lighter than the object by about $1.0/4 = 0.25$ mg. The rider is therefore given a second adjustment to $8.9 + 0.25 = 9.15$ mg, and a second L-r.p. is estimated from two short-swing readings: -1.0 , $+0.2$. The L-r.p. is then $(-1.0 + 0.2)/2$, or -0.4 division. This agrees closely enough with the 0-r.p. so that the weight of the object may be taken as $10.350 \text{ g} + 9.15 \text{ mg} = 10.3592 \text{ g}$. Occasionally, if a poor approximation is used for the sensitivity, a third adjustment of the rider may be necessary.

The short-swing method permits all computations to be made mentally, and the chances of determinate error are much less than for the method of long swings.

7D. ERRORS IN WEIGHING

Considering the sensitivity of the balance, it is not surprising that the weighing process is beset with many sources of error. Efficient use of the balance requires a knowledge of these sources of error and of how they may be avoided. Errors in weighing are most conveniently classified into two groups, random and determinate.

7D.1. Random Errors

The operator. Some errors associated with the operator are so obvious that they hardly need mentioning. Misreading of weights, miscalculation of rest points, careless handling of samples, and many other improper techniques may result in errors varying from very small to very large. The precautions necessary for avoidance of these are equally obvious; the worker must develop and use those techniques necessary for accurate weighing. No balance, no matter how good, can be any more accurate than its user.

Defective balances. If a balance is worn or abused, or if it is out of adjustment, pointer readings may not be reproducible and the precision may be much impaired. There are simple tests that quickly reveal defects in the balance, and simple adjustments or repairs may often be performed by the ordinary laboratory worker. The balance experiments at the end of this chapter are designed to reveal such defects.

Electrification. Static charges may be built up on glass, porcelain, or other insulating surfaces by wiping or brushing. If the charge is great, swings may be extremely erratic. This effect is most perceptible at low humidity, and with objects of large surface. Where met only occasionally, electrification may be avoided by wiping the object with a slightly damp lintless cloth or chamois; the object should then be allowed to stand half an hour in the balance case so as to reach equilibrium with the atmosphere before being weighed. Where electrification is consistently troublesome, the use of ultraviolet light or a radioactive material will cause ionization of the air in the balance case, and promote the discharge of the object. It is stated that electrification causes no trouble if the relative humidity is maintained above 45% (H5).

Temperature gradients. There should be no appreciable temperature gradients within the balance case, or convection currents may occur. These cause drafts against the pans, which may lead to erroneous weighings. It has been found that an error of about 0.2 mg is caused per degree difference between an ordinary porcelain crucible and the balance case (A2). The practice of resting one's hand against the balance case in weighing should be avoided, since this warms the case. It is particularly important that all objects placed on the pans should be at room temperature. This is one good reason for never handling objects directly with the hands, for the objects may be appreciably warmed. To place hot articles anywhere inside the balance case for cooling is extremely poor practice, since this may cause expansion of some parts of the balance that may be slow to recover.

The balance itself should be placed in a room that is fairly uniform in temperature, away from all sources of heat or drafts. Sunlight should

never be allowed to fall on, or even near, the balance. If one side of the beam is at a different temperature from the other, the arm-length ratio may be appreciably changed, causing error. Errors due to temperature gradients are symptomized by drifting rest points and erratic pointer swings.

Interaction of sample or container with water or other components of air. All substances tend to adsorb water onto their surfaces. The extent and rate of adsorption depend upon the specific nature of the adsorbing material and its surface, and also upon the relative humidity and temperature of the surrounding atmosphere. Most important, if either the humidity or temperature changes, the amount of adsorbed water changes, and a particular object therefore changes in weight.

With container materials such as glass, porcelain, platinum, and other metals, adsorption is slight and causes no appreciable error in ordinary quantitative analysis. This is not so, however, if the analyst is concerned with small differences in the weight of containers with large surfaces (e.g., gas density bulbs). In such cases, the most satisfactory expedient is to air-condition the balance room. The use of a counterpoise (i.e., an identical container in the other pan) often provides adequate compensation, but it is seldom perfect; adsorption depends upon too many complex factors to permit the assumption that objects of identical dimensions adsorb equally. A desiccant in the balance case is of questionable value.

With sample materials, adsorption is often great enough to cause serious error. Not only are most such materials finely divided, but many are hygroscopic or even deliquescent. Furthermore, there may be reaction with other components of the air. Strongly reducing substances may react with oxygen and change weight. Basic substances may absorb CO_2 . In all such cases the samples are best weighed in closed containers. If the concern is to keep out moisture alone, only a good closure is necessary. If other components of the air are reactive, it may be necessary to evacuate the vessel or to fill it with an inert gas. Modern dry boxes are large enough to hold balances and other equipment; if necessary, they permit preparation, weighing, and processing of reactive materials under an inert gas atmosphere.

7D.2. Determinate Errors

The three principal sources of determinate weighing error are (1) inequality in lengths of balance arms, (2) weights, and (3) air buoyancy. With proper techniques, these errors may be compensated or corrected for, as described below.

7D.2a. Inequality in lengths of balance arms. If the two arms of a

balance are not equal, the mass of an object may not be considered identical with that of the weights required for counterbalancing, when the direct method of weighing is used. Thus if L_r and L_l are the respective lengths of the right and left arms of the balance, and if an object of true mass, m , is placed in the left pan and counterbalanced by weights, m_r , in the right pan, then, from the law of moments

$$mL_l = m_r L_r \quad \text{or} \quad m = m_r \frac{L_r}{L_l} \quad (7.3)$$

The mass of the object, therefore, may not be taken to be the same as that of the weights unless $L_r/L_l = 1$ (i.e., unless the arm lengths are equal).

In ordinary balances the lengths of the arms usually differ by less than 1 part in 25,000, which is negligible in ordinary analyses. With direct methods of weighing, inequality of the arms seldom gives errors greater than this, provided that (1) the object is always placed on the same pan, preferably the left, and (2) the same balance is used throughout the analysis. Failure to observe these two precautions may magnify the error to appreciable proportions, as the following example shows.

Example. Sample weights are usually obtained as relatively small differences between the weight of a container and the weight of the container plus sample. Suppose that the correct weight of a container is exactly 50 g and that it is directly weighed in the left pan of a balance with $L_r/L_l = 1.00 \dots + 1/25,000$. The apparent weight of the container is therefore 49.9980 g. Now suppose that a sample weighing exactly 1 g is added to the container, making the correct weight 51.0000 g. If the container plus sample is also weighed on the left pan of the same balance, the apparent weight is 50.9980 g. The apparent weight of the sample, obtained as the difference between the two erroneous apparent weights, is 1.0000 g, which is the same as the true sample weight.

Suppose, however, that the container plus sample had been weighed on the left pan of another balance, for which $L_r/L_l = 1.00 \dots - 1/25,000$. The apparent weight of container plus sample would have been 51.0020 g. The apparent weight of sample alone would then have been 1.0040 g, 0.40% greater than the true value.

There are two weighing methods for eliminating the error due to unequal arm lengths. Both take more effort than the direct method, and are not used unless the absolute weight of an object is required with high accuracy, as in the calibration of weights or volumetric equipment.

Weighing by substitution. The object is placed on the right pan and counterbalanced with a tare in the left pan. A *tare* is simply ballast that is used to balance the object; the weight of the tare is not measured, and it may be composed of any stable material. Lead shot is frequently used, although sometimes a second set of weights may be employed. When the tare is adjusted to balance the object, the r.p. is determined. Then, leaving the tare intact, the object is removed and replaced by

known weights until the tare is counterbalanced to the same r.p. as before. In this process, the object has simply been replaced by an equal mass of known weights, and the object weight is therefore identical with the known weights. Knowledge of the weight and lever arm of the tare is unnecessary.

Double weighing. The object is placed on the left pan and weighed directly, taking its weight as the sum of the weights (m_r) in the right pan. Then, the object is placed on the right pan and weighed directly, taking its weight as the sum of weights (m_l) in the left pan. If the balance arms are unequal, one of these weights is less than the true weight by a slight amount, and the other is correspondingly larger. Hence, by averaging the two, the errors cancel and the true weight, m , is obtained (see Supplement, p. 657).

$$m = \frac{m_r + m_l}{2} \quad (7.4)$$

7D.2b. Errors in weights. Weights change in value, owing to corrosion and wear. It should never be assumed that a set of weights is correct without checking. For student work, where weighing errors of a few tenths of a milligram are tolerable, the following procedure is suggested to minimize weighing errors. (1) Check the weight set, including rider and chain. Procedures suitable for student use are given in Exps. 7.4 and 7.5 (pp. 89, 90). (2) Use the weight set systematically, so that errors in weights cancel out. This is possible, since the weight of a gram sample is always obtained as a difference between two weighings. With a little foresight, it is possible to duplicate integral weights above 1 g on both weighings; errors in these weights then cancel when the difference is taken.

For exact work it is necessary to calibrate each weight in a set, for it may not be assumed that the true mass is equal to the denomination. Calibration is also required even for ordinary analytical work if it is desired to use weights that have not been adjusted within required tolerances. (Calibration procedures are discussed in the Supplement, p. 657.)

7D.2c. Error due to air buoyancy. When an object is placed in the balance pan, the net downward force on this pan is that due to the mass of the object minus that due to the buoyancy of air on the object. Similarly, the net downward force on the weights in the other pan is that due to the mass of the weights minus the upward buoyant force of the air on the weights. When the object is balanced by the weights in air, it is these two net forces that are equal.

$$\begin{aligned} m_o - \text{buoyancy on object} &= m_w - \text{buoyancy on weights} \\ m_o &= m_w + (\text{buoyancy on object} - \text{buoyancy on weights}) \end{aligned} \quad (7.5)$$

The true mass of the object, m_o , is referred to as the *weight in vacuum*. The mass of weights required for a counterbalance in air, m_w , is referred to as the *weight in air* of the object. It may be seen from Eq. 7.5 that the true mass of an object is not equal to its weight in air unless the buoyancies on object and weights happen coincidentally to be equal. The term in parentheses in Eq. 7.5, known as the *buoyancy correction*, represents the quantity that must be added to the observed weight in air to give the true weight in vacuum. In ordinary chemical analysis, where only the percentage of a substance is usually determined, buoyancy effects are usually negligible. Buoyancy corrections are significant only when the absolute weight of an object is accurately required, and even then, only when the densities of the object and weights are considerably different. (The calculation of buoyancy corrections is performed in the Supplement, p. 658, and reasons for the negligibility of the corrections in most cases are pointed out.)

7E. OTHER TYPES OF BALANCES

Many other kinds of balances and accessories are used in quantitative work. The chain balance is described in this section, since its use by students is mounting. (Other kinds of balances are described in the Supplement, p. 660.)

One type of *chain balance* is shown in Fig. 7.4. This balance differs in two principal respects from the ordinary rider balance. The rider goes up to 1.0 g, being set at 0.1-g intervals in V-shaped notches on the beam. Weights less than 0.1 g are added by means of a chain assembly. One end of the chain is hung from a knife-edge or jeweled pivot point on the right side of the balance beam; the other end is attached to a hook that travels along a vertical column. The column is graduated uniformly from 0 to 100 mg, and may be read to the nearest 0.1 mg with a vernier scale, one type of which is shown in Fig. 7.5. The hook is made to move by turning the wheel on the lower right side of the balance case; in this way, the length of the chain that hangs from the beam may be varied. The chain is usually made of gold, and is very uniform, so that its weight is strictly proportional to its length. The deviations from linearity for a good chain are less than 0.1 mg, provided that it is installed without twists, and provided that the looped part is always well below the points of support. In some models the chain is not attached to a column but is wound on a rotating dial.

With a chain balance, only integral weights are required for the weight set, and weighings may be performed much more rapidly than with the ordinary rider balance. The trouble and expense of maintaining fractional weights are eliminated. Another useful feature of most chain

types is that the 0-r.p. may be moved by moving the chain reference mark with controls operated from the outside of the balance case; this is very convenient for the single-swing method of weighing.

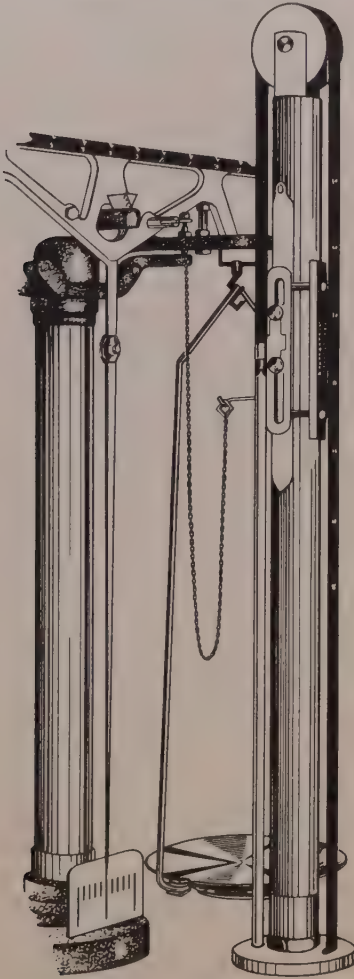


FIG. 7.4. A Chain Balance

7F. RULES FOR USE OF THE BALANCE

The following rules are to ensure accuracy in weighing, to prevent abuse, and to prolong the life of the balance.

1. Balance case, pans, beam, and weights should be scrupulously clean. Use lintless cloth and a camel's-hair brush for cleaning.

2. All controls should work easily. The sensitivity should be 2–4 div/mg, and the 0-r.p. should be within a half-division of scale center.

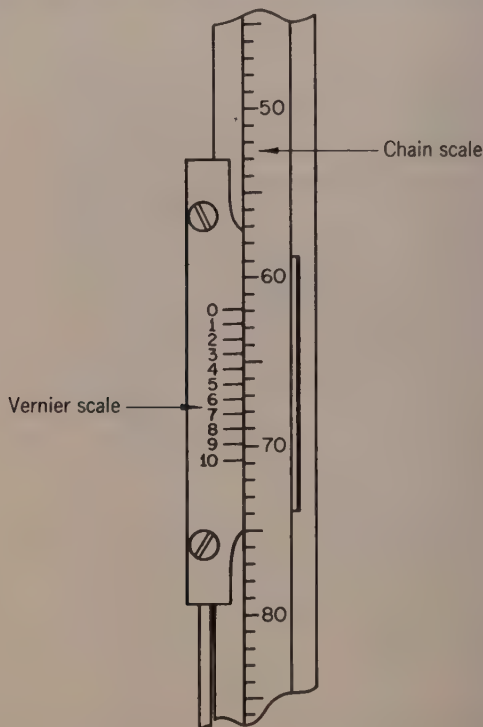


FIG. 7.5. Chain Scale and Vernier—Reading for chain weight is 61.8 mg.

3. Never exceed the maximum load, which is 100 g for most balances.
4. Never handle weights or any part of the balance with the fingers, since perspiration may initiate corrosion. Weights should never be placed anywhere except on the balance pan or in the weight box.
5. Never handle objects to be weighed with the fingers; handling may both moisten and warm the object.
6. Never place hot objects in the balance case.
7. Never place samples directly on the pan; use suitable containers.
8. In freeing the balance, first lower the beam, and then the pan arrests. In arresting, first arrest the pans as the pointer passes through the center of the scale, and then arrest the beam.
9. Never change mass on the pans unless the balance is arrested.
10. Determine the 0-r.p. at each sitting.
11. The object should be placed in the left pan, and weights in the right. Balances should never be changed during an analysis.

12. Center the masses in the pans to as great an extent as possible.

13. Use weights systematically, especially if calibration corrections are not applied. (a) Always return each weight to its own position in the box. (b) Use foresight in selecting weights, so that errors in the large integral weights may cancel out. (c) Never change weights during an analysis. (d) At counterbalance, sum not only the weights in the pan, but also sum the vacancies in the box.

14. Leave the balance arrested, clean, closed, covered, and unencumbered. Never leave heavy loads on the pans for a long time; this may cause permanent distortion of the beam.

15. Report all defects to the instructor. Suggestions for servicing balances and weights are given in the Supplement (p. 665).

7G. EXPERIMENTS WITH THE BALANCE*

Each balance is given a general servicing every few years by the instructional staff. The following experiments are designed to reveal maladjustments that may occur between servicings. Whenever a defect is encountered, the student should report it to the instructor, who will verify it. Any adjustments that cannot be made in class are listed by the instructor and repaired when convenient. After repairs are made, the user should be notified, preferably by a note left on the balance floor. The student should make no adjustments of any sort except with the consent of the instructor.

The second purpose of these experiments is to acquaint the student with his balance, and to provide assurance that his weighing technique is acceptable. It is very important that this be done before time is invested in the analysis of unknowns.

Experiments 7.1, 7.2, 7.3, and 7.4 (or 7.5) are recommended for all students. Experiment 7.6 may interest the professional chemist. Experiment 7.7 offers an over-all check on the student's equipment and weighing technique. Pertinent data and results for each experiment performed should be recorded in the notebook. Careful organization of the notebook *prior* to performance of this work is well worth the student's effort (p. 68).

EXPERIMENT 7.1. OPERATION OF THE BALANCE

The following items should be checked.

1. The whole balance, including the case and floor, should be perfectly clean.

*A 45-minute instructional motion picture on weighing is available from the Television Laboratory, University of Wisconsin, Madison, Wisconsin.

2. The balance should be level, on a sturdy bench that is free of vibration and away from drafts, direct sunlight, heat sources, and corrosive fumes.

3. The windows should work easily.

4. The pointer should be straight and should move close to the scale, but without touching it.

5. The rider control should hold the rider securely, and should position the rider accurately and easily anywhere on the beam. If the rider is of the wire type, it may need straightening. Leave the rider on zero.

6. If there is a chain, it should be easily movable from a few milligrams below zero to a few milligrams above 100 mg. In the 100-mg position, sight along the chain to ascertain that it is untwisted and hangs freely. Leave the chain on zero.

7. The beam arrest should work smoothly. To test for proper adjustment, first lower the pan arrests; the pointer should not jump when the beam is then gently lowered. Leave the balance arrested.

8. The pan arrest should work smoothly, and should be adjusted so as barely to touch the pans, not to lift them. To test for proper adjustment, arrest the pans; the pointer reading should not change when the beam is then raised or lowered.

9. With the rider and the chain on zero, free the balance. Swings should be smooth, and should decrease in amplitude by no more than a few tenths of a division per swing.

10. Inspect the following devices, if they are included with the balance. (a) The control for the chain vernier should be snug but smooth. The zero should be set near the center of its range of travel. (b) The control for moving the pointer scale should be snug but smooth. The scale center should align with the pointer when the balance is arrested. (c) The damping device should work easily.

EXPERIMENT 7.2. DETERMINATION OF THE ZERO REST POINT

If the 0-r.p. is not within 0.5 division of scale center, have the instructor adjust the balance. Using the method of long swings, make three determinations of the 0-r.p., arresting the balance after each determination. If the range of the three determinations is greater than 0.4 division, repeat until this precision is attained.

EXPERIMENT 7.3. DETERMINATION OF SENSITIVITY

Determine the sensitivity at no load as the difference between the 0-r.p. and the r.p. with the rider (or chain) at 1 mg. Use the method of long swings. The sensitivity should be 2-4 div/mg. Find the sensi-

tivity at a load of 5 g by placing the 5-g weight in the left-hand pan and the 2-, 2', and 1-g weights in the right pan, and determining the rest points with the rider at 0 and at 1 mg. The difference in these two rest points is the sensitivity at a load of 5 g. Repeat for loads of 10, 20, and 50 g. Plot a sensitivity curve similar to Fig. 7.2 (p. 72) from the experimental data. The sensitivity at 50 g should be at least 60% of that at no load.

EXPERIMENT 7.4. CHECKING THE WEIGHT SET (10-MG RIDER BALANCE)

Whenever a weight set changes hands, the new user should check its accuracy. The following procedure is adequate for student work, and guarantees that weighing errors will seldom exceed 0.5 mg. First, it is verified that weights of the same denomination are identical within required tolerances. Then it is ascertained that larger weights are equal to combinations of smaller ones, within required tolerances. If all members of a set check each other in this way, the set is said to be *internally consistent*. If a weight set is internally consistent within certain tolerance limits, it is almost certain that the weights are absolutely correct within about the same limits. It is highly improbable that the whole set would be proportionately in error by an amount much exceeding the tolerance limits selected.

TABLE 7.1
WEIGHT CHECKS FOR THE 10-MG RIDER BALANCE
(Weights in milligrams, unless otherwise noted)

Determination	Weight in Left Pan	Weights in Right Pan	Tolerance
1.....	10	10-mg rider, R	0.1
2.....	10'	R	0.1
3.....	20	$R + 10$	0.2
4.....	50	$R + 10 + 10' + 20$	0.3
5.....	100	$R + 10 + 10' + 20 + 50$	0.4
6.....	100	100'	0.2
7.....	200	$R + 10 + 10' + 20 + 50 + 100$	0.4
8.....	500	$R + 10 + 10' + 20 + 50 + 100 + 100' + 200$	0.4
9.....	1 g	All fractionals + R	0.4
10.....	2 g	All fractionals + $R + 1$ g	0.4
11.....	2 g	2' g	0.2

Since balance-arm lengths seldom differ by more than 1 part in 25,000, weights up through 2 g may be checked against each other by direct weighing, with errors due to unequal balance arms not exceeding 0.1 mg. Weights of 5 g or larger should be checked by substitution.

For the first determination, place the 10-mg weight in the left pan and the rider at 10 mg. With the method of short swings, ascertain that the r.p. is within 0.1 mg of the 0-r.p.* Repeat this process for the weight combinations shown in Table 7.1. Any weight that exceeds the tolerance should be sought out with the help of the instructor and a set of standard weights, and exchanged for an acceptable weight.†

The 5-, 10-, and 20-g weights may be similarly checked, to ascertain that each is within 2 mg of its denomination. Such a check reveals only gross error in these larger weights, which must be used as suggested on pages 83 and 87 to prevent significant weighing error. It is not feasible to keep large weights within close tolerances when used by students.

EXPERIMENT 7.5. CHECKING THE WEIGHT SET (CHAIN BALANCE)

After the manner of Exp. 7.4, ascertain that the weight combinations of Table 7.2 are equal within the tolerances shown. Any weight that exceeds the tolerance limits should be sought out with the help of the instructor and a set of standard weights, and exchanged for an acceptable weight.† If the rider or chain is in error by more than 0.2 mg, it should be calibrated.

TABLE 7.2
WEIGHT CHECKS WITH THE CHAIN BALANCE

Determination	Weight in Left Pan	Weights in Right Pan	Tolerance (mg)
1.....	1 g	1-g rider, <i>R</i>	0.2
2.....	2 g	1 g + <i>R</i>	0.3
3.....	2 g	2' g	0.2
4.....	1 g	Rider at 0.9 g, chain at 100 mg	0.3

Calibration of the rider. If the rider is out of tolerance, obtain a standard 1-g weight from the instructor and determine the true weight of the rider at 1 g, using the method of long swings. Return the standard weight immediately. Calculate the error of the rider at 1 g, and apply this as a proportional correction on all rider weights, until notified that the rider has been adjusted by the instructor. For example, suppose that the rider at the 1-g position really weighs 1.0005 g. At the 1-g position, therefore, 0.5 mg must be added to the rider reading to obtain the correct weight. If the rider is used in the 0.6-g position, the correction is $0.6 \times 0.5 = 0.3$ mg, and the correct weight is 0.6003 g.

Because of the high accuracy with which the rider notches are ground

*For a balance with a sensitivity of 3 div/mg, 0.1 mg would correspond to 0.3 div.

†Alternatively, the weight may be retained after calibration with a standard weight.

into the beam, it is not necessary to check on intermediate rider positions if the 1-g position is correct. However, if it is suspected that the balance has been abused, checks on a few intermediate positions against standard fractional weights are advisable.

Calibration of the chain. Calibrate the chain only if it is out of tolerance. First, make certain that the chain is untwisted, and that it hangs freely. Obtain a 100-mg standard weight from the instructor, and find the true weight of the chain when it reads 100 mg. Apply a proportional correction, as described for the rider above. Because of the possibility of stretching or distortion, the chain calibration should be checked at two or three intermediate positions with standard fractional weights obtained from the instructor.

EXPERIMENT 7.6. DETERMINATION OF THE BALANCE-ARM RATIO

Place a 50-g weight in the left pan, and obtain its weight by counterbalancing with weights m_r in the right pan, assuming the latter to be correct. Then obtain the weight of the same 50-g weight in the right pan, by counterbalancing with weights m_l in the left pan. From these two weighings, the ratio of the lengths of the balance arms may be calculated from Eq. 7.3 (p. 82), to give

$$\frac{L_r}{L_l} = 1 + \frac{1}{2} \left(\frac{m_l - m_r}{m_r} \right) \quad (7.6)$$

For this ratio, any deviations from unity that exceed 1 part in 25,000 should be reported to the instructor. Such deviations may indicate permanent strains.

EXPERIMENT 7.7. DETERMINATION OF AN UNKNOWN WEIGHT DIFFERENCE

An "unknown" consists of two numbered parts that differ in weight by less than 1 g. With the short-swing method, weigh each part separately. Observe the weighing rules on page 85 very scrupulously.

Calculate and report the weight difference.

This experiment gives a check on weighing technique and on the accuracy of weights below 1 g. For good work, the error of the weight difference should be less than 0.4 mg for the 10-mg rider balance, and less than 0.2 mg for the chain type.

QUESTIONS

Sections 7A, B

1. How would a balance behave if the c.g. lay above the fulcrum?
2. Explain why the rest point is never calculated beyond the nearest 0.1 division.

3. Discuss the effect on sensitivity of each of the following changes, assuming that all other factors remain unchanged.

- (a) Moving the small brass collar on the pointer.
- (b) Moving the nut on the end of the left-hand beam outward sufficiently to change the 0-r.p. by 1.5 divisions.
- (c) Increasing the load on the pans.
- (d) Moving the pointer scale down and increasing the length of the pointer.
- (e) Lengthening the balance arms.
- (f) Constructing the beam with a denser material, but keeping the dimensions unchanged.
- (g) Increasing the distance between the fulcrum and the c.g. of the beam-pointer system.

4. What disadvantages would accompany the effort to increase sensitivity by decreasing the mass of the beam? By increasing the pointer length?

5. Compare the relative merits of the 5-2-2-1 and 5-3-2-1 sequences for weights.

Section 7C

1. With care, the beam need not be arrested while fractional weights are added or taken from the pan. Why?

2. Cite the advantages and disadvantages of using a sensitivity curve, rather than measuring the sensitivity at each weighing.

3. Why are weights obtained with the ordinary analytical balance never computed beyond the nearest tenth of a milligram? (Assume a sensitivity of 2 div/mg.)

4. Why need the sensitivity be only approximately known when the method of short swings is used? What are the consequences of not knowing the sensitivity at all?

Section 7D

1. List simple practices that might reduce weighing errors due to carelessness and oversight.

2. Considering convection currents, would the observed weight of an object warmer than room temperature be greater or less than the true weight?

3. Speculate on the causes of the following phenomena, which are sometimes observed in weighing.

- (a) With the balance pans empty, the rest point drifts slowly.
- (b) The balance swings evenly without the sample, but the pointer swings drift as follows when the sample is in the right pan: -4.4, +2.3, -4.3, +2.3, -4.1, +2.4, -3.9, +2.6, -3.8, +2.7.
- (c) Upon a second ignition, an empty crucible shows a weight increase of several milligrams, the same weights and balance being used.
4. What technique would you use to weigh accurately 0.8-1.2-g samples consisting principally of the following substances: (a) acetone, (b) conc. H_2SO_4 , (c) water, (d) NaOH, (e) Pb shot, (f) NaCl?

5. The left arm of a balance is longer than the right. Is the true weight of an object greater or less than the weight observed by the direct method of weighing?

6. Explain how, with different weights, the observed weight in air of a given object could be either greater or less than the true weight.

7. Each integral weight above 2 g in student sets may be in error by as much as 2 mg. How may this error be avoided in each of the following cases?

(a) A sample bottle with a large excess of sample weighs about 20.6 g, and a student wishes to withdraw an accurately weighed sample around 1 g.

(b) A carefully prepared filtering crucible weighs about 29.7 g. About 1 g of precipitate is to be isolated and weighed in this crucible.

8. Why should the 0-r.p. be frequently determined?

Experiments

1. Explain the action by which the chain adds weight to one side of the balance.
2. The graduations on the chain dial or column are linear. For such linearity to apply, what must be true regarding the location of the curved part of the chain?

3. To measure the sensitivity at a 10-g load, a student puts the 10-g weight into the left pan, and the 5-, 2-, 2', and 1-g weights plus rider at 1 mg into the right pan. The difference between this L-r.p. and the 0-r.p. is then taken as the sensitivity at a 10-g load. Explain how this technique requires fewer weighings than that of Exp. 7.3. Why is this shorter technique not acceptable?

4. If each weight is adjusted within 0.2 mg of its denomination, what is the maximum weighing error that could occur in the weight of a 1.9890-g sample, as measured on a 10-mg rider balance? Is this error very probable? What would the tolerances of Table 7.1 (p. 89) have to be, if this reasoning were followed?

5. In Exp. 7.5, the chain is found to be out of tolerance, being too light by 2.0 mg for a reading of 100 mg. Examine your chain balance, and explain the mechanism by which the chain may be adjusted to be within tolerance.

6. A chain that is too heavy by several milligrams is adjusted so that the error is less than 0.2 mg. After adjustment, the 0-r.p. drifts for about an hour, and a check reveals that the chain is still too heavy by 0.5 mg. Explain.

7. Assuming that the objects in Exp. 7.7 weigh around 45 g, explain why the weight of one of these objects cannot be accurately found and reported for grading. Assume that the procedures of Exp. 7.4 or 7.5 have been used to check the weight sets.

PROBLEMS

Sections 7A-C

1. Assume that the maximum error in determining a rest point is 0.1 division on the scale, and that a difference of two rest points is involved in obtaining the weight of an object. Show that the sensitivity must be at least 2 div/mg in order to keep the weighing error below 0.1 mg.

2. After a steady state of oscillation is attained, a series of pointer readings is +4.2, -5.6, +3.8, -5.4, +3.6, -5.1, +3.4, -4.9, +3.1, -4.7, +2.9, -4.4, +2.7, -4.2. Show that any five consecutive pointer readings give the same rest point within experimental error.

3. The 0-r.p. of a balance is at -0.6 division on the scale. A weight of 1.8 mg on the right pan moves the rest point to -3.7 divisions on the scale.

(a) What is the sensitivity? *Ans.* 1.7 div/mg.

(b) What is the rest point with 2.7 mg on the right pan? *Ans.* -5.2 div.

(c) What weight is in the right pan if the rest point is at +1.8 divisions on the scale? *Ans.* 1.4 mg less than in the left pan.

4. The sensitivity of a balance is 3.1 div/mg. With the 0-r.p. at the center of the scale, what is the maximum difference in weight that may be tolerated so that the

rest point does not fall off scale (i.e., beyond 10 divisions from the center of the scale)? Why is the practical difference less than this?

5. On the balance of Fig. 7.3 (p. 74), what is the weight of the rider itself?

6. Find the weight of an object to the nearest 0.1 mg from the following data.

Swings of empty balance: -1.5 , $+5.6$, -1.2 , $+5.3$, -1.0 .

Swings of balance with object in left pan, 19.472 g in right pan, and rider at 4.0 mg: $+5.4$, $+0.3$, $+5.2$, $+0.1$, $+5.0$.

Swings of loaded balance, after the rider is moved to 5.0 mg: -4.0 , $+0.8$, -3.7 , $+0.6$, -3.5 , $+0.5$, -3.4 .

7. Find the weight of an object to the nearest 0.1 mg from the following data.

Swings of the empty balance: -1.7 , $+3.0$, -1.5 .

Swings with object in left pan, 16.834 g in right pan, and rider at 2.0 mg: -3.0 , $+1.2$, -2.8 .

Swings of loaded balance when the rider is moved to 1.0 mg: $+3.8$, $+1.2$, $+3.5$.

Ans. 16.8355 g.

8. Find the weight of an object to the nearest 0.1 mg from the following data, taken with an ordinary balance.

Swings of empty balance: -4.7 , $+4.2$, -4.5 .

Swings of balance with object in the right pan, 13.540 g in the left pan, and rider at 7.0 mg: $+1.3$, -5.8 , $+1.2$.

Swings of loaded balance, with the rider at 6.0 mg: -1.5 , $+5.2$, -1.3 .

9. An empty crucible is weighed, a sample is introduced, and the crucible plus sample is weighed again. From the following data, find the sample weight to the nearest 0.1 mg.

0-r.p.: $+1.6$.

L-r.p. for empty crucible, with 11.673 g in pan and rider at 6.0 mg: $+3.9$.

L-r.p. for crucible plus sample, with 12.183 g in pan and rider at 9.0 mg: -2.9 .

Sensitivity of balance at loads of 11–13 g: 3.0 div/mg. *Ans.* 0.5107 g.

10. In Prob. 9, assume an erroneous 0-r.p. of 3.9 (which is identical with the L-r.p. for the empty crucible), and calculate the weight of the sample on this basis. Observe that the correct weight is still obtained. Why is this so? By this method, the work is reduced; the 0-r.p. need not be taken, and the correct weight of the empty crucible need not be calculated. This procedure is recommended when it is known that the 0-r.p. remains constant for the two weighings.

11. In weighing an object in the left pan by the method of short swings and precise adjustment of the rider, two short swings with 13.876 g in the right pan and the rider at 8.4 mg are $+2.6$, $+0.7$. The 0-r.p. is $+0.5$. If the sensitivity is about 3 div/mg, what should be the next adjustment of the rider?

Ans. 8.0 mg.

Section 7D

1. The right arm of a balance is 0.005% longer than the left arm. An object in the left pan requires 46.7623 g of standard weights in the right pan for an exact counterbalance. What is the correct weight of the object? *Ans.* 46.7646 g.

2. The arms of a balance differ in length by 1.0 part in 25,000, the left arm being longer than the right. What is the true weight of an object that weighs 29.8435 g by the direct method of weighing?

3. In the example on page 82, when both weighings are made on the same balance, is the difference exactly 1 g? What is the relative error of the difference?

Ans. No; 1 in 25,000.

4. In a certain weight set, the 1-g and 1'-g weights are identically equal, and so are the 20-g and 20'-g weights. A balance with $L_r/L_l = 1.00005$ is used. Calculate

the apparent difference in milligrams between the 1-g and 1'-g weights when weighed directly against each other. Repeat the calculation for the 20-g and 20'-g weights. Explain how the results indicate that the direct method may be used to check weights up to 2 g, but not the larger integral weights, within tolerances of 0.2 mg.

5. An object is double-weighed. It has an observed weight of 41.8743 g when in the left pan and 41.8761 g when in the right pan. Calculate the correct weight of the object and the ratio of the lengths of the balance arms.

Ans. 41.8752 g, $L_r/L_l = 1.000022$.

6. The distance between the 0 and 1-g notches on the beam of a chain balance is exactly 15 cm. Over what range of distance from the 0 notch must the 0.9-g notch be located, so that the rider error is less than 0.1 mg?

7. One milliliter of water weighs one gram, and one milliliter of air weighs 1.2 mg. Neglecting the buoyancy of air on the much denser brass weights, what would be the apparent weight in air of the one milliliter of water? What is the relative error if the buoyancy correction is neglected?

Ans. 0.9988 g; 1.2 p.p.t.

Experiments

1. From the following data, give the calibration correction of the 1-g rider, and give the correct weight when the rider is at 0.4 g. The 0-r.p. is -0.5 division. With the rider at 1.0 g, and a standard 1-g weight in the left pan, the L-r.p. is +2.1 divisions. The sensitivity is 3.2 div/mg.

Ans. -0.8 mg; 0.3997 g.

2. From the following data, give the calibration correction of the chain, and give the correct chain weight when its reading is 67.3 mg. The 0-r.p. is +0.8 division. With the chain at 100.0 mg, and a standard 100-mg weight in the left pan, the L-r.p. is -3.6 divisions. The sensitivity is 2.7 div/mg.

3. Derive Eq. 7.6 (p. 91). Discuss the assumption that the weights in the weight set are correct, and show that, even if the weights are in error by as much as 50 mg (at 50 g), the error in the ratio of the lengths of the balance arms would still be insignificant.

8 REAGENTS AND GRAVIMETRIC TECHNIQUES*

This chapter presents elementary techniques and apparatus that are especially useful for gravimetric analysis. Classification is made according to techniques rather than equipment, which is described with the operations in which it is used. The following suggestions may be useful.

(1) The student should scan this chapter and familiarize himself with the content rather early in the semester. The time for detailed study is not until these techniques are ready to be applied to a particular experiment; then study should be very critical. (2) When the operations are encountered for the first time, it is well to practice some of them on dummy samples before applying them directly to unknowns. The few extra minutes required for such practice are amply repaid by fewer mishaps. (3) Only the manipulative aspects of the operations are described. The theoretical aspects are dealt with in other parts of the book. (4) The fundamental techniques are described in a general way, applicable to many different determinations. Any particular problem to which these methods are applied should be thoroughly studied and understood, for the peculiar properties of a system and its chemistry may require modifications or additions to these techniques.

*A 45-minute instructional film on gravimetric techniques is available from the Television Laboratory, University of Wisconsin, Madison, Wisconsin. A 20-minute supplementary film on filtration with the Gooch crucible and filter paper is also available.

8A. REAGENTS

8A.1. Grades

Chemicals are manufactured in several grades of different purity.

Commercial-grade or technical chemicals are not generally used for laboratory reagents. This grade is produced largely for industrial use, and may contain many impurities.

U.S.P.-grade chemicals are purified to pass certain tests indicating the absence of certain kinds of impurities. These chemicals may therefore contain appreciable amounts of impurities not tested for. The tests are given in detail in the U.S. Pharmacopoeia (**U8**). In general, the purity of the U.S.P. grade is not as high as that of reagent and C.P. grades; but U.S.P. chemicals are adequate for many laboratory purposes.

Chemically pure (C.P.)-grade chemicals are of indefinite purity, but are usually purer than the U.S.P. grade. In fact, many C.P. substances are prepared by almost the same processes as the reagent grades, and are almost as pure. Such chemicals are specially purified according to standards set by the individual manufacturer. Because these standards vary, the designation is often ambiguous and is becoming obsolete.

Reagent- or analyzed-grade chemicals are manufactured, purified, and tested to ensure that the content of certain impurities is below specified maximum limits, set by the Committee on Analytical Reagents of the American Chemical Society (**A8, R13**). The labels on containers for such reagents often specify the maximum limits of the impurities tested for. The manufacturer checks each batch before packaging, and guarantees the correctness of the label. It is strongly recommended that only reagent-grade chemicals be used in analytical work. In many analytical applications, of course, other grades are satisfactory and may be used. However, since only small amounts of chemicals are used in analysis, the saving is hardly great enough to compensate for the possibility of confusion and for the greater space required to store more than one grade in the laboratory.

Primary standard-grade chemicals meet all the requirements of reagent-grade chemicals, and in addition are known to contain a certain amount (usually very close to 100%) of the principal substance. Some such substances are listed in Appendix IVA (p. 911). Often, special methods of purification are required to prepare primary standard chemicals. General characteristics and uses for primary standard chemicals are given in Sec. 14A.5 (p. 233). The number of commercially available primary standards is constantly increasing.

8A.2. Purification

The analytical chemist no longer has to spend a large part of his time and effort in purifying reagents. Chemical manufacturers are extremely appreciative of the requirements of the analytical chemist, and do their utmost to meet these needs. Today many analytical reagents need only be dried or treated very simply in order to be used as primary standards.

In some applications, such as trace analysis, even reagent-grade chemicals are insufficiently pure, and must be further refined. In such cases special methods, unique for each reagent, must be used. A general summary of purification procedures is given by Kolthoff and Sandell (K18). Hillebrand *et al.* describe purity tests and preparation of many common reagents (H8).

8A.3. Preparation, Storage, and Use

Appendix IVA gives a list of the reagents used for the experiments in this book. Practical information on properties and the preparation of special solutions is also given (Appendix IVB).

Reagents purchased in small containers are placed on the laboratory shelves in the original containers. When purchased in bulk, the chemicals must be put in special containers for dispensing in the laboratory. Solids are usually put in wide-mouthed glass-stoppered bottles. Liquids or solutions are put in narrow-mouthed glass-stoppered bottles for ease in pouring, or into semipermanently located bottles fixed with siphons for withdrawal. Because of their greater resistance to chemical action, Pyrex glass bottles are preferable to soft glass. Reagents that react with glass are kept in containers coated with a resistant material (wax for hydrofluoric acid, sodium hydroxide, etc.). Plastic bottles, made from polyethylene, are used widely, but they have limitations because the plastic is permeable to gases (CO_2 , O_2) in air (T1).

Reagents that must be protected from air or moisture require special equipment for storage. Gas reagents are dispensed from the cylinders in which they are purchased, either directly or by pipeline to various locations in the laboratory. When only small amounts are required, and commercial cylinders are not available, a gas may sometimes be generated in a combination storage generator, such as the Kipp.

Certain precautions must be observed by the users of reagents. (1) Only a slight excess over the required amount should be poured from the reagent bottle to the user's container. Because of the danger of contamination, a reagent should never be withdrawn from its bottle by the introduction of a pipet. (2) Also, because of the possibility of contamination, an unused portion of any reagent, once withdrawn, should never be returned to the container, but should be disposed of in

an appropriate manner. Insoluble solids should be put into waste jars, and soluble solids or solutions flushed down the sink with a copious amount of water. (3) Spilled materials should be cleaned up immediately. (4) Key reagents, especially ones used by many individuals, should be tested for contamination before use on samples. Such tests can usually be made very quickly and simply, and may save hours or days of wasted effort.

8A.4. Water

Water is used in analysis in larger amounts than any other chemical, and even traces of impurities may therefore cause relatively large errors. For this reason only distilled water is used in chemical analysis.

Even distilled water may contain impurities. (1) Soluble or insoluble impurities may be carried over from the boiler with the distillate, owing to frothing, bumping, or spraying in the still. Such materials may also be introduced into the water after distillation, from pipes or containers. (2) Dissolved gases from the atmosphere (CO_2 , NH_3 , O_2 , etc.) are always present in ordinary distilled water. (3) Organic impurities may come from dust or from lubricants in valves and other parts of the piping system. Each of these types of impurities may cause trouble in certain analyses, and special means may be necessary for their removal. Directions for such special treatment, together with tests for adequate purity, are usually given with the directions for analysis. In general, to prepare good water, it is necessary to redistill it first from alkaline permanganate to oxidize organic matter, and then from a slightly acid solution to remove ammonia.

To prepare standard acid and base solutions, CO_2 -free water is usually necessary. Water in small batches (1–5 l) may be quickly and entirely freed from CO_2 and other gases by being boiled for a few minutes. This is the preferred laboratory method. Such water rapidly reabsorbs gases, and must be protected from the atmosphere during cooling, storage, and later handling. Large batches of distilled water may be freed from CO_2 by bubbling purified air through them for several hours. The air itself is first purified by being passed through H_2SO_4 to remove NH_3 , then through NaOH to remove acid spray and CO_2 , and then through a moist filter to remove dust and spray.

Since distilled water is usually produced continuously, its impurities may fluctuate considerably. Water from the same still that is good one day may not be so the next. If the water contains enough impurities so that a correction must be applied to the analysis, it is important that corrections be determined on the same batch of water as that used in the analysis itself.

8B. HEATING

A variety of heat sources is available, each with its own uses and advantages.

Gas burners are the most common individual source of heat in the laboratory. The object to be heated is placed directly in or above the flame and is supported by rings, clamps, or triangles (Nichrome, clay, or silica). The principal advantages of gas burners are mobility and convenience; the disadvantage is that uniform control of the heat requires constant attention. Uneven heating causes bumping and loss of liquids. Strong gas currents promote loss of powdery materials when these are heated in uncovered containers. Wire screens or asbestos pads are sometimes used to distribute heat more evenly.

The following maximum temperatures may be obtained in covered platinum crucibles with different types of burners: Bunsen, 1000°C; Tirrell, 1100°C; Meker or Fischer, 1200°C. The maximum tempera-

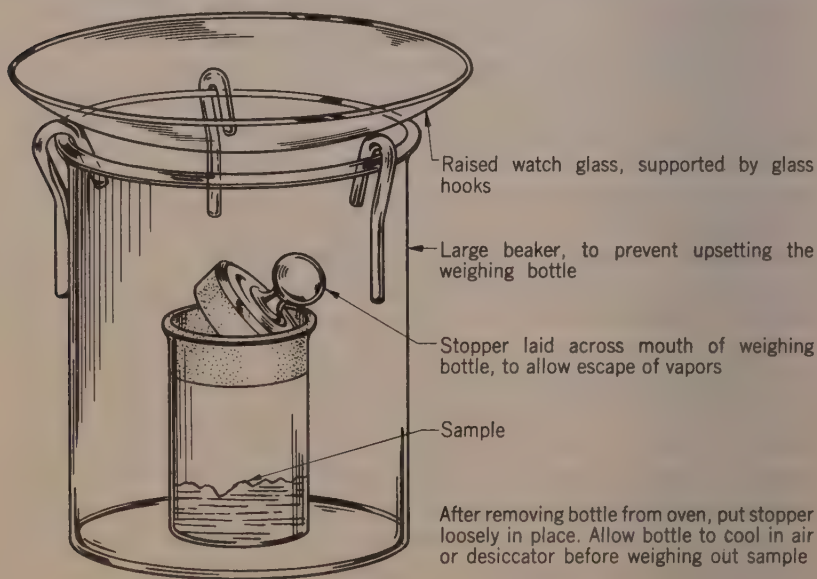


FIG. 8.1. Drying a Sample in an Electric Oven

tures attainable in covered porcelain crucibles are 200–300°C lower than these. The following color scale is a useful indication of the temperature of an object: dull red, 600–800°C; cherry red, 800–1000°C; orange, 1000–1100°C; yellow, 1100–1200°C; white, over 1200°C.

The electric hot plate is a less intense and more controllable source of

heat than the gas burner, and may be used to heat liquids up to 200–250°C with less danger of bumping.

Electric ovens are thermostatically regulated and may be used to heat objects at controlled temperatures up to 250°C. Samples that are wet or likely to give off corrosive fumes are first evaporated, dried, or decomposed outside the oven, so that the wiring and interior will not be damaged. Samples should be put in covered containers to prevent their contamination by flakes from the interior of the oven or from spilling by fellow workers. Small objects, such as weighing bottles, should be put in a beaker to prevent their being upset (Fig. 8.1).

Oven space is always at a premium, and every effort should be made to conserve it. Objects should be grouped together and against the rear and side walls so that any object may be removed without disturbing others. The fronts and centers of shelves should be kept clear or only thinly populated with objects. At the end of the period, all articles must be removed from the ovens, so that space is available to the next class. Equipment remaining overnight may be confiscated. Under no circumstances should ovens be used to dry out glassware or other pieces of equipment.

Thermostated electric furnaces are used for controlled temperatures up to 1250°C. Electric furnaces are used with the same conventions described for ovens. In addition, especially at high temperatures, access must be restricted, and the doors must not be opened and closed frequently. A schedule of “open” and “closed” times should be posted next to each oven. Students should plan their work to adhere strictly to such schedules, especially in large classes, or desired temperatures may never be attained. Glass containers soften and melt above 450°C, and should not be heated in furnaces.

Air baths are used to control heat applied with burners. Figure 8.2 shows three types of air baths to accommodate small crucibles. The insulating layer of air prevents bumping by reducing the rate at which heat reaches the contents of the inner crucible. Also, the outer container acts as a radiator that, together with the insulating air layer, gives fairly even heat distribution. The air bath is neither as controllable nor as efficient as the electric oven or furnace, and is only used in their stead to carry out evaporations of corrosive liquids in hoods. To prevent loss by spattering, evaporations of solutions containing H_2SO_4 or HF must be made in an air bath.

A *large hot plate* for community use is made by placing a shallow tray over steam coils. This is suitable for heating or evaporation at low temperature over a long time, since practically no attention is required. Large sand baths or steam baths are also used, but they are not so clean

as the hot plate. This equipment must be used with the space-saving considerations described above for ovens.

Infrared lamps are used to heat very small (drop-sized) samples. When such small volumes of solution are heated with ordinary burners, the droplets may literally burst, owing to the high rate of application

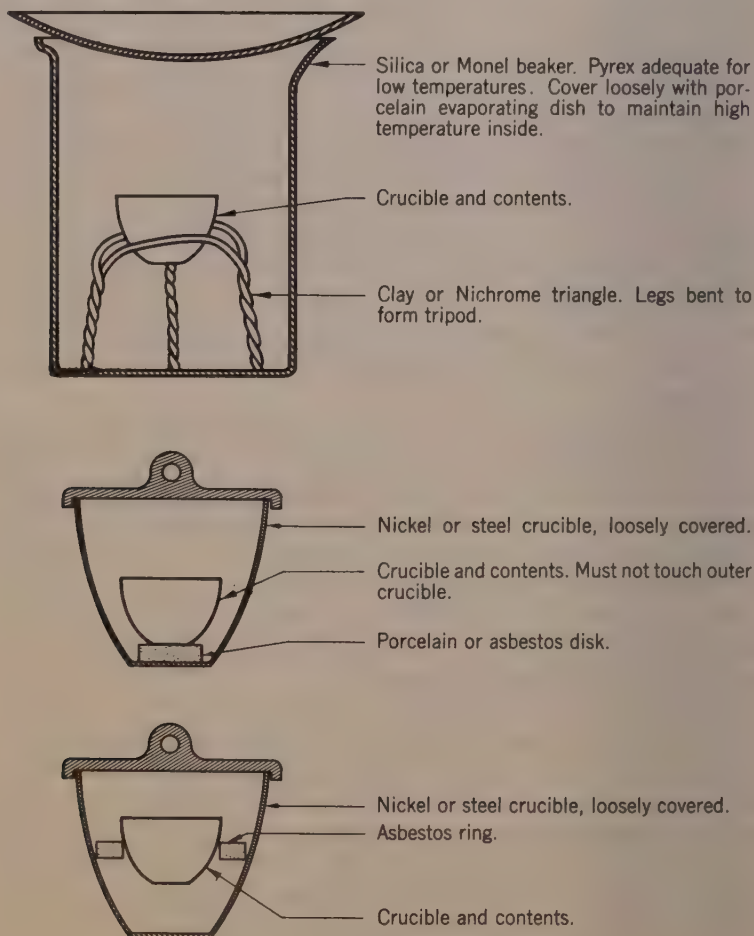


FIG. 8.2. Three Types of Air Baths

of heat. With the infrared lamp there is no great tendency toward superheating, since the rate of heating is limited by the absorption of the infrared energy, which in turn is proportional to the volume of the sample.

8C. DRYING

Most materials are dried with one of two aims: (1) to remove variable amounts of loosely bound water, or (2) to convert the material into a weighable form. The first is accomplished at rather low temperatures and is commonly performed on samples to be analyzed. The second requires high temperatures and is frequently used on gravimetric precipitates.

8C.1. Drying of Samples

The conventional procedure for drying a stable, solid sample is to heat it for 2 hours at 105–110°C. For small samples, the technique of Fig. 8.1 is suitable. For an unknown sample, the 2-hour drying treatments must be repeated until constant weight is reached. Samples that have received this treatment are said to be *oven-dried*. Unless students are informed to the contrary by the instructor, all samples of the elementary course should be oven-dried; also, it may be assumed that constant weight is reached in 2 hours at 105–110°C.

When samples containing loosely bound water are not dried, the amount of water held is dependent upon temperature, humidity, and history of the sample; consequently the sample weight is not reproducible. Oven-drying removes this water and gives a more definite sample weight.

If it is not possible to achieve constant weight by oven-drying, it may be that the sample is unstable to heat, or that the water is too tightly held to be driven off rapidly at low temperatures. Other drying procedures may then be used, provided that they do not decompose the sample. Substances unstable to heat may be *air-dried*, that is, allowed to dry in air or in a desiccator at room temperature. Organic materials are often so treated. Sometimes special drying conditions are used, depending upon the specific nature of the sample. Stable samples may of course be dried at high temperatures. Occasionally, samples are *analyzed as received*, without drying treatment of any sort. Because all these different drying methods exist, the drying method used must be specified in reporting the result of an analysis.

8C.2. Drying and Ignition of Precipitates

Precipitates are usually separated from solution by filtering. If filter paper is used, the process of converting to a pure dry compound involves burning off the filter paper, for which a fairly high temperature is required. Even if a filtering crucible is used, *ignition* to a high temperature may still be necessary to dry the compound completely, or to con-

vert it to the proper weighing form. Many substances are precipitated and filtered as one compound, but are converted to another for weighing by heating at a high temperature. Calcium, for example, is often precipitated as the oxalate, which is not weighed as such but is decomposed by heat to the carbonate or oxide for weighing. Some precipitates, such



1. Flatten paper at top, with one-thickness side toward you. Do not squeeze so that precipitate is forced out.



2. Fold upper corners in toward center.



3. Fold top over. Then fold bottom, which contains the bulk of precipitate, up onto the top, as shown in next step.



4. Fold sides in gently, so that precipitate does not burst paper.



5. Press folded paper into crucible, with precipitate against bottom.



6. Crucible and paper ready for ignition.

FIG. 8.3. Folding Paper for Insertion into Crucible before Ignition

as Fe_2O_3 or Al_2O_3 , need high temperatures to remove the last traces of water.

Most ignitions are performed at $500\text{--}1000^\circ\text{C}$. Porcelain crucibles are satisfactory up to 1000°C , provided that the samples contain no alkalies, alkali carbonates, or fluorides. Above 1000°C , porcelain glaze melts,

and silica or platinum crucibles are necessary. At such temperatures corrections may be necessary for loss in weight due to slight volatilization of the crucible (B30).

Precipitates that are unstable at high temperatures may sometimes be dried by washing with ether, alcohol, or acetone, and then oven- or air-dried. For instance, Mg may be determined as $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, which is rinsed with alcohol-ether and air-dried. AgCl is sometimes rinsed with alcohol and air-dried. When metals are precipitated with organic compounds, the products must be dried at low temperatures to avoid decomposition.

8C.2a. Ignition of precipitates on filter paper

1. Remove the paper and precipitate from the funnel as described on page 124. The moist paper is folded as shown in Fig. 8.3, and pressed into a crucible that has been brought to constant weight by the same heat treatment as is intended for the precipitate.

2. Dry the paper and precipitate in the crucible. This is best done by allowing the crucible to stand overnight. If there is not time for this, set up for charring, and dry the paper before charring, as indicated in Fig. 8.4. In drying, heat should be applied to the top, rather than to the bottom, so that the contents will not spatter. If there are no corrosive fumes, the crucible and paper may be dried in the electric oven.



Crucible rests in inclined position, with bottom squarely against one leg of the triangle.

For drying paper, remove lid and apply heat to upper rim of crucible.

For charring, put lid in position shown. Heat crucible carefully from the bottom, moving burner in direction of arrow until flame is tangent to bottom. If paper bursts into flame, smother with lid.

FIG. 8.4. Charring Filter Paper before Ignition

3. Char the paper as shown in Fig. 8.4. Under no circumstances should the paper burn, since precipitate may be lost with the combustion gases. For the same reason, the burner flame should not sweep over the mouth of the crucible. Care is needed to prevent loss in this part of the process. After the paper is charred, burn off the carbon by heating strongly with free access to air.

4. Ignite. Set the crucible upright, cover, and heat for the specified length of time. An electric furnace is better than the burner for this step; for the preceding steps, however, a burner should be used. Unless otherwise specified, crucibles should always be covered during ignition. Also, the triangle used to support the crucible should be very clean, since many oxides and impurities melt into the crucible glaze at temperatures far below the melting point. This may cause imperceptible chipping of the crucible or sticking to the triangle.

5. Store the crucible in the desiccator for cooling after ignition. Remove the crucible from the heat source and allow it to cool for about half a minute after the red glow disappears; then place it in the desiccator. If ignition has taken place in a furnace, the outside bottom of the crucible should be lightly brushed before it is weighed, to remove grains of refractory material that continually drop to the furnace floor.

8C.2b. Ignition of precipitates in filtering crucibles. This is simpler than ignition on filter paper. The crucible and contents should be dried overnight or in an oven before ignition, to prevent spattering. After drying, the procedure is essentially the same as in step 4 above. If ignition is to be done with a burner, it is often desirable to place the filter crucible inside a larger one, to prevent direct action of burner gases on the precipitate.

8C.3. The Desiccator

The common *desiccator* (Fig. 8.5) is a covered glass container, designed for storage of small objects in a dry atmosphere. It must be pointed out that the efficiency of an ordinary desiccator as a method of drying is very poor, since it takes a long time for the moisture to diffuse from the object through the air to the desiccant. The purpose of a desiccator is to maintain an already dried object indefinitely in a dry condition.

It is not true that an object gains no moisture in a desiccator. When the object is put into the desiccator, some undried air from the room enters also. During the time required for cooling, both object and desiccant compete for the moisture introduced with the air. Even after the usual 30–40 minutes, the desiccator air contains much more water than would normally be in equilibrium with the desiccant, and the object absorbs some of this water. Figure 8.6 shows the rate of change of water-vapor pressure in a desiccator (B21). For this reason, the desiccator should be opened as infrequently as possible, kept open only as long as necessary, and objects should be lowered into it with as little disturbance of the air as possible.

It has been shown that even moderately hygroscopic materials actu-

ally gain moisture when stored in the desiccator (K5). Therefore, vessels containing powdery materials that have a tendency to absorb water should always be covered for storage in a desiccator. The cover reduces the moisture taken up during the initial period of high humidity existing

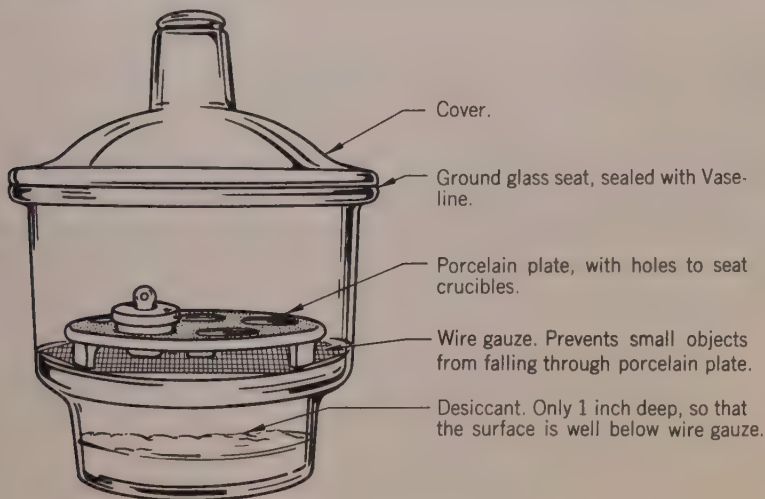


FIG. 8.5. The Desiccator

shortly after introduction of the object, before the desiccant has had time to act. This precaution is necessary even with highly efficient desiccants. Covers are desirable for another reason; they prevent light powders from being blown out by the inrush of air if the desiccator lid is not carefully removed.

If the object has been heated, it is desirable to introduce it to the desiccator while still very hot (several hundred degrees). Convection currents are then set up, which hasten the removal of moisture in the air.

Hot objects cool slowly in a desiccator. If the desiccator is used to store an object while cooling prior to weighing, adequate time must be allowed. In weighing an ordinary porcelain crucible after ignition and cooling in the desiccator, errors around 0.8 and 0.4 mg were found after cooling periods of 30–60 minutes and 60–90 minutes, respectively. Even after 90–120 minutes, errors around 0.2 mg were found (A2).

Moist materials should never be put in a desiccator, but should be oven- or air-dried first.

For substances that have a high affinity for water a very efficient desiccant is required, but even this is useless unless the foregoing practices are followed.

Some desiccators are equipped with stopcocks, so that the air may be

pumped out immediately after the object is introduced. Then the curve of Fig. 8.6 not only starts at a lower pressure, but also drops faster because of the greater rate of diffusion of water to the desiccant at reduced pressure. Metal (aluminum) desiccators are now being used. Compared to glass desiccators, these have the advantages of low cost, low breakage, and rapid cooling of objects. Most desiccants must be placed in a glass or porcelain dish so that they do not contact and corrode the metal. There are many other special types of desiccators.

Preparation of the Desiccator

1. Remove the old desiccant, discarding or regenerating it as directed by the instructor. (Some drying agents react violently with water, and should be flushed carefully down the sink rather than thrown into waste jars.)

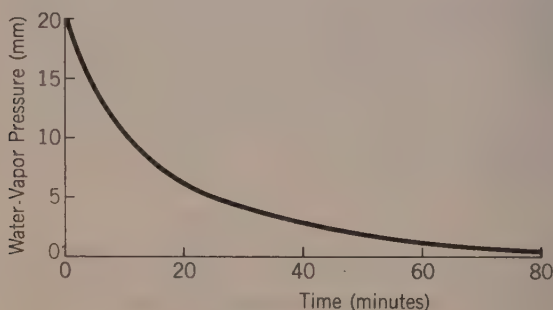


FIG. 8.6. Water-Vapor Pressure in a Desiccator—Air in desiccator initially saturated with water. (Reprinted from H. S. Booth and L. McIntyre, *Industrial and Engineering Chemistry, Analytical Edition*, 8, 148 [1936], Fig. 2, by permission of the publisher.)

2. Wipe off the old grease with a paper towel, wash with soap and water, and dry with a clean towel. No lint should remain after drying. The porcelain plate should be spotlessly polished and kept so.

3. Charge with desiccant to a depth of one inch only. In the filling process, avoid the dusting of desiccant onto the sides of the desiccator. Use a small beaker as a scoop to transfer desiccant into the desiccator. Bring the tip of the beaker close to the inside bottom of the desiccator and let the desiccant slide gently out of the beaker. Do not let the desiccant fall through any appreciable height. When a sufficient amount is added, level the desiccant, and wipe off any dust from the upper inner walls of the desiccator. Then insert the wire gauze and porcelain shelf.

4. Put a thin band of Vaseline around the ground-glass area, put on the cover, and rotate it back and forth through a small angle (without

lifting and breaking the seal) to distribute the Vaseline. If the proper amount of lubricant is used, the contact area is clear. Carefully wipe excess Vaseline from the inner and outer edges with a paper towel, without smearing.

Handling the Desiccator

1. To open the desiccator, place it squarely upon the desk top, anchor it to the desk top with one hand, and slowly slide the cover to one side with the other hand. If the pressure inside is less than atmospheric, the sliding should be done very slowly, stopped as soon as air begins to hiss into the vessel, and not continued until pressures are equalized.

2. To carry the desiccator, place the palms of the hands on opposite sides, with index fingers under the lip. The thumbs should hold the lid on, so that it will not pop off if the inner pressure is accidentally greater than atmospheric.

3. If possible, objects should be put into the desiccator when hot. Wait about a half-minute after any red glow disappears, and then put the object on the porcelain shelf, being very careful not to touch the glass, which might crack. Put the desiccator cover on, but leave a small opening to the air for another half-minute. Then slide the cover into place and seal. If the desiccator is closed too soon, pressure may build up inside and pop the lid off. As the contents cool a slight vacuum develops inside, pulling down the lid and giving a good seal.

8D. WEIGHING

8D.1. Techniques

Samples are seldom weighed right on the pan of the balance. The weight of a sample is usually found as a difference between the weight of the container with and without the sample. Two methods are used.

The *direct method* of weighing is carried out as follows: (1) The weight of the empty container, placed in the left pan, is found to the nearest 0.1 mg. (2) Weights equal to the weight of the sample desired are then added to the right pan. (3) The sample is then added to the container until a counterbalance is reached. It is best to add slightly over the required amount of sample, and then to remove portions with a spatula until a portion is reached whose removal puts the weight of the sample somewhat under the required amount. Part of this last portion is then returned to the container by tapping the spatula so that granules fall off in very small amounts. Unless a certain quantity of sample is desired, it is too time consuming to try to adjust the weight of the sample to give an exact counterbalance, which is best obtained by adjusting the

rider or chain. The weight of container plus sample is then determined to the nearest 0.1 mg. (4) The weight of the sample is the difference between the weights of the empty container and the container plus sample.

The direct method is useful only for stable substances that do not change on exposure to air. The method is generally used when the material may be weighed into the vessel in which the next step of the analysis is to be carried out. The direct method is particularly appropriate for obtaining a certain weight of sample, as may be necessary in preparing a standard solution of a certain concentration.

The *indirect method* is carried out as follows: (1) The weighing bottle with excess sample is weighed to the nearest 0.1 mg. (2) The sample is then transferred with a spatula from the bottle to the vessel in which the next step of the analytical process is to be performed. Everything that goes out of the bottle must go into the receiving vessel. It is better to underestimate the amount to be transferred, because a second portion may always be added if the first is not large enough; it is poor practice to transfer from the receiving vessel back to the weighing bottle if the first portion is overestimated. (It is helpful to use a comparison sample of approximately known weight, so that the desired amount may be estimated visually.) (3) The weight of the weighing bottle after removal of the sample is determined to the nearest 0.1 mg. (4) The weight of the sample is determined as the difference in weight between the bottle with sample and the bottle minus sample.

The indirect method is useful for weighing out substances not stable in air, for the sample may be kept in a closed container during most of the process. It is the preferred method if there is leeway in the desired sample size, so that any weight within a rather liberal range is satisfac-

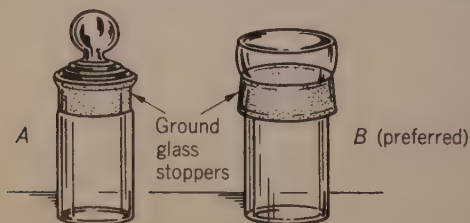


FIG. 8.7. Two Common Types of Weighing Bottles

tory. (This is usually the case.) It is not appropriate if a certain quantity of sample is needed. Transfer of the sample after weighing need never be made, since the sample may be put in any vessel. The indirect procedure is generally recommended over the direct one. Provided that the weighing bottle contains enough material, n samples may be ob-

tained with only $n + 1$ weighings by the indirect method, whereas $2n$ weighings are required by the direct method.

8D.2. Containers

Weighing bottles vary in size up to 100 ml. Two common types are shown in Fig. 8.7. Type *B* is preferred; there is less chance of loss due either to adherence of the sample to the stopper when removed, or to material on the ground-glass surface being blown out when the stopper is inserted. Such bottles may be used for both solid and liquid samples.

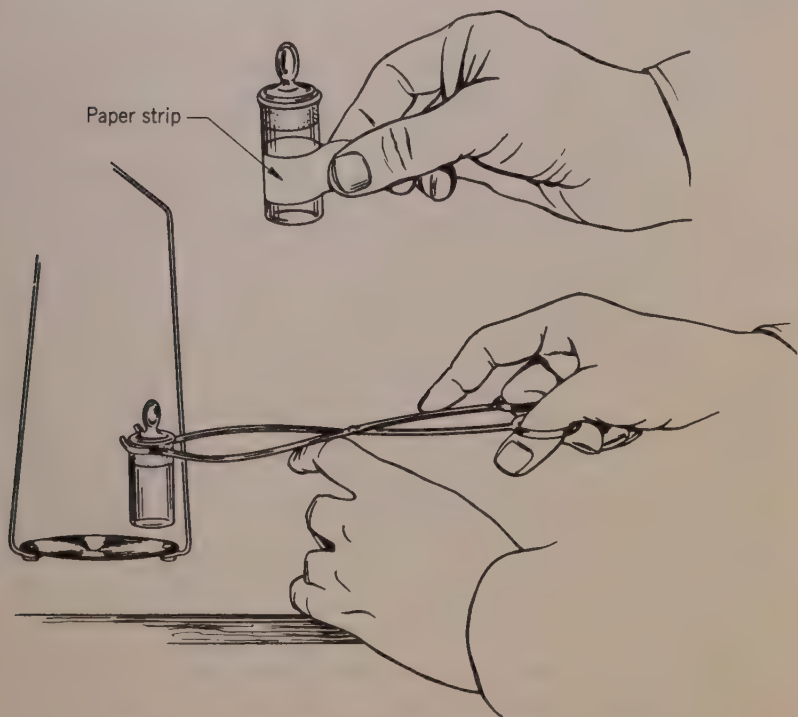


FIG. 8.8. Two Methods of Handling Weighing Bottles

There are many other special types of containers designed for solid, liquid, or gaseous samples, or for preventing contact with air, or for other special purposes. Odd-shaped containers that are likely to fall from the balance pan are attached with a wire to the lower hook of the pan stirrup. Liquids must always be stored and weighed in closed containers, because of evaporational losses. Usually, liquid samples are weighed out by the indirect method, from a weighing bottle with a ground-in dropper.

After being cleaned, containers or objects to be weighed should be handled as infrequently as possible with the fingers. Small bottles may be handled by the methods shown in Fig. 8.8. Small objects may sometimes be handled best with forceps. When it is necessary to use the fingers, they should be clean and dry. It is sometimes convenient to grasp objects through a few layers of clean towel. Chamois finger cots (single-finger sleeves) are even better, if much handling must be done.

8D.3. Transfer of Samples

Small amounts of solids may be transferred from one container to another with a clean, highly polished *spatula*. The container with sample should always be held over the receiving vessel, which should rest upon black glazed paper if possible, so that losses may more easily be detected and recovered. In another method (usually not preferred), the bottle is tipped with the mouth down and rotated back and forth through a small angle so that the solid slides slowly from the bottle and down the sides of the inclined receiving vessel. In quantitative transfers, materials should never fall from any appreciable height, because of the danger of loss by dusting or splashing.

Once weighed out, samples are not transferred in the dry state unless such a step is absolutely necessary. Use of a camel's-hair brush to effect transfer is not good practice, because of the danger of loss due to static electricity. A sample that has been weighed out into a small container may usually be transferred in the wet way, by flushing the material into the receiving vessel with a stream of water from the wash bottle. If the receiving vessel is narrow necked (such as a volumetric flask), a funnel should be used to make the transfer. If the solid is insoluble, a rubber policeman may be necessary to complete the transfer.

8D.4. Achievement of Constant Weight

Whenever a substance is dried or ignited before being weighed, some assurance is needed that the process is complete. The following technique of going to *constant weight* gives this assurance. The substance is treated and weighed. Then the treatment is repeated and the substance reweighed. If the second weight is the same as the first within experimental error, it may be assumed that the treatment is complete. If the weights are different, the treatment is repeated until two consecutive weights are identical within experimental error. If constant weight cannot be achieved, the source of error should be sought. The desiccator should be used to store the object between successive treatments, especially if considerable time elapses between them.

To achieve accuracy, weighing technique should be made as reproducible as possible. (1) Make weighings quickly after removing the object from the desiccator, to reduce moisture uptake. Use the short-swing method. If the object weight is known approximately, place the proper weights on the balance before opening the desiccator. (2) Containers should be covered while they are being weighed. Loose closures are better than none at all. (3) Standardize times in the desiccator, if possible. (4) When igniting a precipitate, bring the empty crucible to constant weight by the same treatment as is intended for the precipitate.

8E. DISSOLUTION

The solution or decomposition process often depends specifically upon the nature of the sample, and is therefore not very systematic. For reasons given in Chapter 2, preparation and solution of the sample are deemphasized in the introductory course. The samples for the elementary experiments in this book dissolve or decompose rather easily.

It is well to point out that the preparation and solution of a sample are often subject to greater error than is the actual process of measuring the amount of sought-for substance itself. Where this is the case, it is quite pointless to make several determinations on aliquots of a single solution prepared from a single sample. To obtain a proper idea of the precision of the method, several samples should each be run through the preparation and solution steps, as well as through the determination itself.

Most processes for putting the sought-for constituent into solution fall into three classes, according to the solvents used.

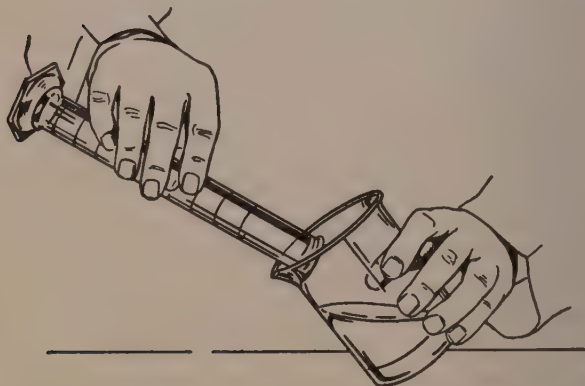
Solution in water. Water suffices to put some samples into solution, or at least to put the sought-for constituent into solution. These procedures are very simple. If the whole sample is soluble, it is weighed into a vessel suitable for the next step in the analysis (i.e., beakers for precipitations, flasks for titrations, etc.). The proper amount of water is then added to the sample. Because of the danger of loss by splashing, water or reagents are never allowed to fall into a container, but are added by the methods of Fig. 8.9. If the reagent is added with a pipet, the stream is directed against the sides of the beaker rather than directly into the contents.

During a quantitative analysis, sample solutions should never be boiled unless absolutely necessary, because there is almost always loss by spray or spattering. If it is the purpose simply to heat the solution, maintenance just below boiling is almost as effective as boiling, but much safer. If it is the purpose to evaporate the solution, see page 131. If a solution must be boiled in a beaker, it should be covered closely with a

watch glass and filled not over one-third of its capacity (Fig. 8.10). Vapors can escape through the void between the beaker spout and the watch glass. For extended boiling, a flask should be used instead of a



Tip of glass rod held close to, but clear of, beaker contents, unless rod is to be immersed in solution after pouring.



Beaker held inclined, so that liquid trickles slowly down side of beaker without splashing.

FIG. 8.9. Pouring Liquid Reagents

beaker, and a *short- or bent-stem funnel* inserted to reduce losses (Fig. 8.10). Such funnels are particularly useful for adding reagents to samples that froth or effervesce. On completion of the heating, these covering devices must be thoroughly rinsed and the washings added to the solution.

Solution in acids. Samples that do not dissolve in water often yield to acids. Although some processes require special equipment, most are

carried out in the beakers or flasks in which the next analytical step is to take place. If the acid causes effervescence or if the solution must be boiled, a flask is preferred, as in Fig. 8.10. If it is necessary to dissolve the sample in a beaker, and if acid causes effervescence, the acid should be added with a pipet, keeping the beaker covered as closely as possible with a watch glass. The violence of evolution may sometimes be reduced by adding water to the sample, and then adding the acid to the slurry instead of to the dry sample. Occasional gentle swirling during the solu-

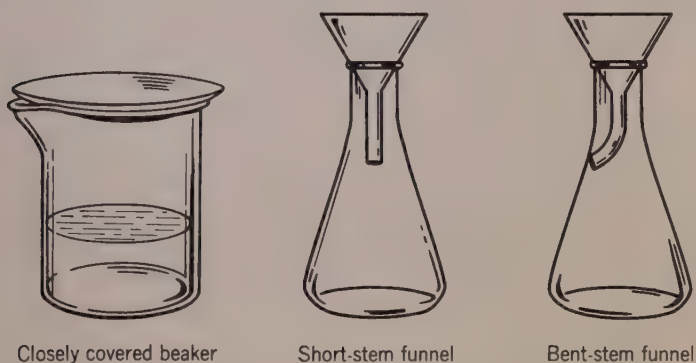


FIG. 8.10. Covering Vessels to Prevent Loss on Boiling

tion process may greatly increase the rate of solution. After the solution process is complete, any covering devices must be carefully rinsed and the rinsings added to the solution.

Fusions. If the sought-for substance is not attacked by acids, it may be converted to a soluble substance by a fusion, which is a chemical reaction carried out in the dry or molten state at high temperature. The compound added to react with the sample is called a *flux*. For quantitative analysis, fusions are almost always carried out in crucibles. The crucible should preferably be inert, but, if reactive, must not contain any of the sought-for substance. Although directions for fusions are often detailed and highly dependent upon the nature of the sample and the analysis, there are certain general precautions that should be observed. (1) The sample and flux should be finely ground and intimately mixed. Many reactions in the solid state are notoriously slow because of the limited contact between reactants. Everything feasible should be done to increase this contact. (Mixing may be done in the crucible, provided that it is not too full.) (2) To reduce chances of loss, the crucible should never be more than half full. A cover is almost always necessary. (3) Heating should be gradual, especially at the beginning, to allow quiet escape of water or other gases. In general, the

temperature should be kept at the minimum specified; too high a temperature may cause excessive reaction with the crucible, or may cause the flux to decompose before it can react with the sample. (4) The fused mass, or *melt*, is dissolved after solidification. The solution process may be very slow if the melt is allowed to solidify to a small, compact button in the bottom of the crucible. To avoid this, the crucible is taken up with the tongs while the contents are still molten, and rotated and tilted during cooling so that the melt wets the crucible walls almost to the top. This distributes the solidified mass as a thin layer over the interior of the crucible, presenting a greater surface for solvent action later.

8F. PRECIPITATION

Precipitations for gravimetric analysis are usually performed in beakers, to facilitate the quantitative removal and recovery of the precipitate. The vessel should be less than two-thirds full when the precipitation is complete. In order to reduce loss, and to achieve as pure and filterable a precipitate as possible, the following techniques are generally used.

The precipitant is usually added to the solution of the sought-for substance in the beaker; the reverse procedure involves a quantitative transfer of the sought-for substance and is seldom used. In order to avoid contamination through high local concentrations of precipitant, the reagent is added slowly, with continuous stirring, and in as dilute a solution as practicable. Addition is made with a pipet, or from a buret permanently mounted to deliver into the beaker if the addition must occur uniformly or during more than 5–10 minutes. The precipitant is seldom added from a graduate or beaker, unless the solution is very dilute.

Stirring during precipitation is usually performed manually, with a glass stirring rod 2–3 inches longer than the depth of the beaker. To prevent scratching the beaker, the rod should not scrape or hit against the sides of the vessel in the stirring process. A motor-driven stirrer is useful for procedures of long duration. If permissible, the precipitation is done in hot solution. It is desirable to stir occasionally during cooling.

In the precipitation process, there must never be splashing of any sort. The reagent is never allowed to fall into the beaker contents from any appreciable height, but is added as described on page 113. Stirring must be smooth and deliberate. Solutions are never boiled during precipitation. Beakers should be free of scratches, lest some precipitate lodge in them and be lost.

A 5–10% excess of reagent should be used, over the amount estimated

from the approximately known or guessed-at composition of the sample. Very large excesses of precipitant should be avoided. When the estimated amount of reagent has been added, the precipitate should be allowed to settle, and then a few more drops of precipitant should be added to the clear supernate. If no precipitate forms, it may be assumed that the process is complete, and the filtration may be begun. The precipitate usually settles sufficiently for the test to be made by the end of the digestion process. When the precipitate does not settle sufficiently to allow the test before filtration, the test should be performed on the first portion of the filtrate. It is highly desirable to test for complete precipitation before filtration. If precipitation is found to be incomplete after filtration has begun, it is difficult to continue the determination, since the precipitate is distributed among so many vessels.

Before being added to the sample, the water and reagents should be tested for the absence of sought-for or interfering substances. A simple test, though not certain, is to add the precipitant to a mixture of all the substances used in the precipitating solution, except the sample. Absence of a precipitate indicates pure reagents.

8G. DIGESTION

After precipitation is complete, the precipitate is usually not filtered immediately, but is allowed to *digest* for some time. The beaker should be covered with a watch glass to prevent contamination. If evaporation is not desired, the glass should cover the beaker closely; if evaporation is desired, the watch glass should be raised with glass hooks, or a ribbed watch glass should be used. Digestion at elevated temperature is best performed on a hot plate. The solution should not be boiled. If digestion extends over a long time, evaporational losses must be replenished regularly. Digestion is not always necessary, or even desirable; the specific directions for the case at hand should be closely followed.

8H. FILTRATION AND WASHING

The purpose of *filtration* is to separate a precipitate from its mother liquor. The precipitate is retained and concentrated on the filter, while the mother liquor passes through. Washing is required to separate the last traces of mother liquor from the precipitate. Before a filtration is begun, a test for complete precipitation should be made, if possible. Also, the receiving vessel should be very clean, so that particles passing the filter may be detected and recovered, and so that a test of the filtrate for complete precipitation may be made, if necessary.

8H.1. Filtration through Papers

The advantages of *paper filters* are cheapness, availability, and high retentivity. However, paper filters are being replaced by filtering crucibles in many instances, owing to the following disadvantages. (1) Paper filters are attacked by many solutions, such as concentrated alkalis, acids, and some oxidizing agents. (2) Even if not attacked chemically, papers still show a tendency to disintegrate, especially if a large volume of solution is passed. (3) Papers break under low stress, and do not readily allow use of suction to speed filtration. (4) For accurate work, papers cannot be quantitatively dried to constant weight but must be burned off. They cannot be used with precipitates that are unstable at red heat or reducible by gases liberated in burning. For moderately accurate work, however, some precipitates may be collected on a weighed paper, dried at low temperature, paper and precipitate weighed, and the weight of precipitate found by difference.

Choice of type of filter paper. The size of the paper should be such that it is filled by the precipitate to only one-third or less of its total depth. Ashless filter papers are used for quantitative determinations. An ashless paper under 12 cm in diameter leaves a residue weighing less than 0.1 mg on ignition; ash weights of such papers are marked on the box. The grades shown in Table 8.1 are only a few of the many offered by manufacturers. Some papers are available not only as circles, but also as sheets, rolls, and strips. The pamphlet from which

TABLE 8.1
ASHLESS FILTER PAPERS

MANUFACTURER'S NUMBER				POROSITY	SPEED	TYPE OF PRECIPITATE
Schleicher, Schuell	Whatman	J. Green	Munktell			
589-black ribbon..	41	801	0	Coarse	Rapid	Coarse or gelatinous
589-white ribbon..	40	802	00	Medium	Medium	Ordinary crystalline
589-blue ribbon..	42	803	00H	Fine	Slow	Fine crystalline

some of these data are taken contains other useful information, including a table of recommended papers for about 400 different analytical precipitates (S3).

Cellulose ester filters with closely controlled pore sizes down to 5 μ are available at nominal cost. The finer of such filters enable the separation of solute particles of different sizes. Proteins, viruses, and bac-

teria can be separated from smaller solute molecules. Thus, a filter with a $10\text{-m}\mu$ pore size retains congo red but passes solutes of lower molecular weight. The filtration rate is of course slow for such fine filters, but is still fair ($1\text{ ml per min per cm}^2$ at 700 mm pressure for the $10\text{-m}\mu$ filter).

For some gelatinous or finely divided precipitates, the speed of filtration rapidly diminishes as the pores of the paper become clogged with

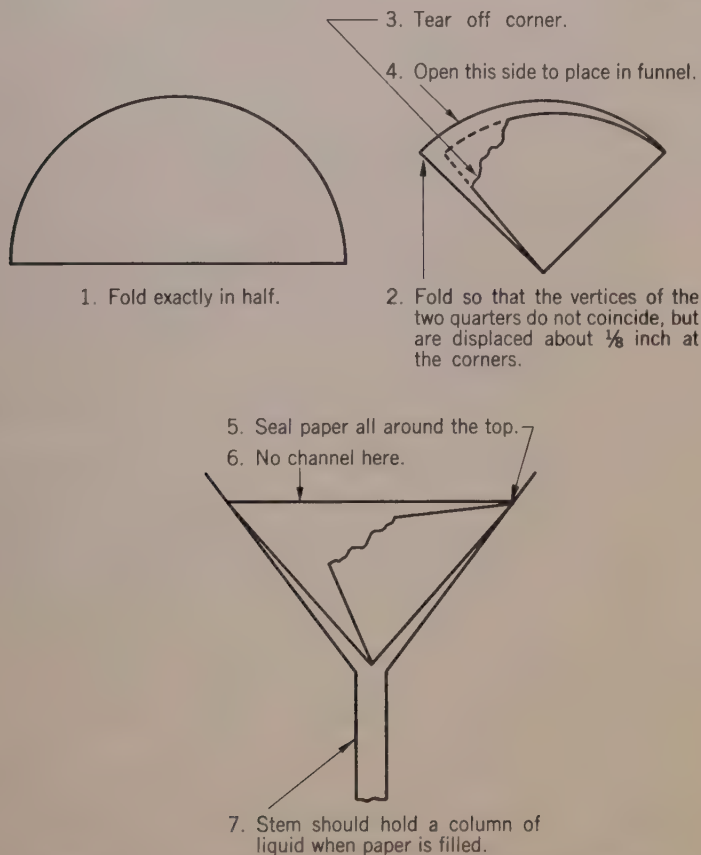


FIG. 8.11. Folding and Inserting a Filter Paper in a Funnel

precipitate. In such cases, filter pulp may increase the speed; the particles of precipitate are held to the surface of the pulp fibers and do not clog the pores. *Filter-pulp* tablets which disintegrate when put in solution are commercially available. Pulp is most useful when added before precipitation, but it is also helpful when added afterward. There are other advantages to the use of pulp. (1) Retentivity is increased and fine particles have less tendency to pass the filter. (2) Cleaning of the

beaker is facilitated by the scouring action of the pulp. (3) Washing is more efficient, since the precipitate does not pack and channel. (4) After ignition, a more finely divided, less lumpy product is obtained, which reaches constant weight more rapidly, and reacts better with fluxes in subsequent fusions. (5) Decrepitation during ignition is diminished.

Inserting the paper into the funnel. The paper is folded and inserted into the funnel as shown in Fig. 8.11. When folded in this way, the paper cone has an angle slightly greater than that of the glass funnel, and fits the walls of the funnel around the circumference but not at the apex. This leaves space between the paper and funnel, allowing free flow of the filtered liquid. The folds should be made very lightly, especially at the apex, to avoid weakening the paper. To seal the paper into the funnel, the paper is placed in the funnel, moistened, and the upper part pressed gently and carefully against the glass with the fingers.

If the paper is properly inserted into the funnel, there is no channeling of air between the paper and the glass, and the funnel stem fills with a column of liquid when the paper is filled with water. The suction created by the water column increases the rate of filtration. The outside corner of the paper is torn off to give a good, unbroken fit between the upper circumference of the paper and the glass. Channeling of air may occur along the fold if this corner is not torn off.

Sometimes the stem does not fill readily with a column of water, especially if the stem is greasy or too wide. In this case, the finger should be held over the end of the stem until it does fill with water. Any air driven up out of the stem should be allowed to escape by breaking the paper-to-glass seal at the three-thickness side; afterward the paper should be resealed to the glass. If the stem does not hold the column of liquid when the finger is removed, the funnel should be cleaned and a new paper folded.

For very flocculent or bulky precipitates, the paper is sometimes folded in a fluted fashion, which gives more filtering surface.

Pouring off mother liquor. As much of the mother liquor as possible is decanted through the filter without disturbing the precipitate in the beaker, so that the major portion of the liquid may be filtered rapidly, before the precipitate begins to clog the filter. Figure 8.12 outlines the pouring operation. It is well to keep the funnel always fairly full of liquid. After the funnel is filled, it may be necessary to interrupt the pouring and to set the beaker on the table while waiting for the filter to empty. When pouring is interrupted, the beaker is not turned upright immediately, since there is then a tendency for a drop to adhere to the outside of the spout and to run down and be lost. Instead, the beaker is tipped back only slightly and the clinging drop is transferred to the rod by touching the rod to the beaker spout. The drop adhering to the

end of the rod is then removed by touching it to the three-thickness side of the filter paper. The rod is laid across the top of the beaker, with the wet end resting on the spout.

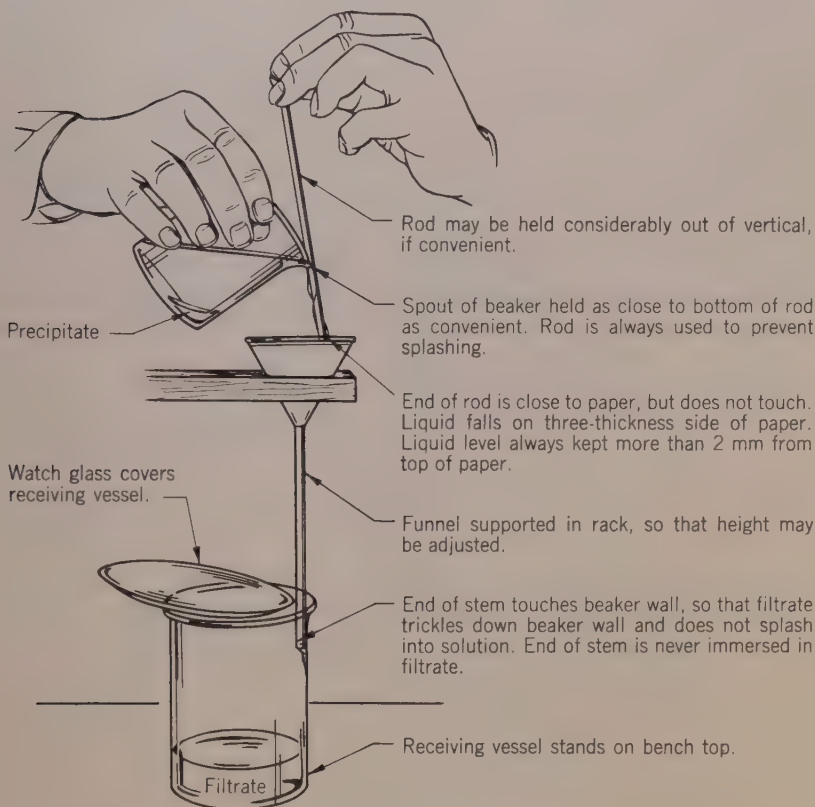


FIG. 8.12. Pouring through the Filter

During filtration, the filtrate is carefully examined for traces of precipitate. If there are any, the filtrate is passed through the same paper again and caught in another clean beaker. If precipitate persists in coming through, the paper is too coarse, or the precipitate is too fine for quantitative filtration. As soon as enough filtrate accumulates, it should be checked for complete precipitation by adding excess precipitant. If precipitation is not complete, consult the instructor.

Washing by decantation. It is advantageous to wash some precipitates by decantation, since better contact may be achieved between precipitate and wash liquid. To wash by decantation, the beaker is set upright

on the table, and the bulk of precipitate adhering to the sides is washed onto the bottom with a stream from the wash bottle. The precipitate and the liquid are swirled, the precipitate allowed to settle for a few minutes, and the supernate then poured through the filter, leaving most of the precipitate behind. This process is repeated once or twice more,

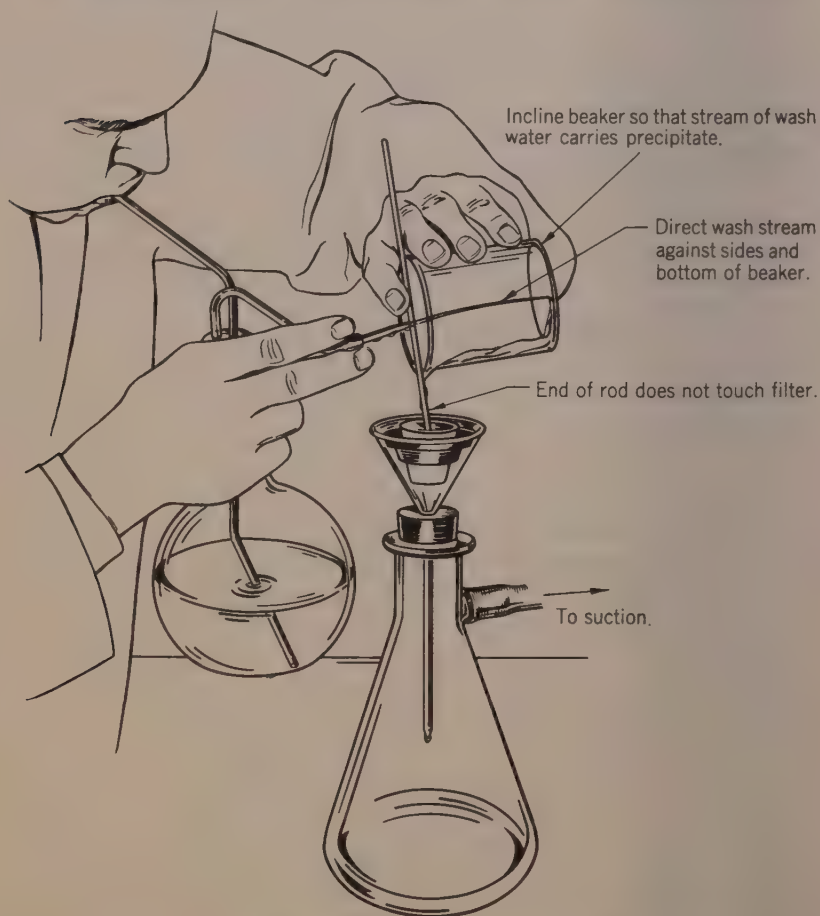


FIG. 8.13. Transferring a Precipitate into a Filtering Crucible

using enough wash liquid per portion to give a depth of 1–2 cm. The filter is allowed to drain before the next wash portion is added.

Some precipitates may be washed better by decantation than others. Gelatinous precipitates that clog the paper are best washed as much as possible by decantation (four to five times), with only the final washing made on the paper. On the other hand, if the precipitate settles very

slowly there is not much advantage to washing by decantation. Washing by decantation requires fairly large volumes of wash liquid, and cannot be used effectively if the volume must be kept to a minimum.

Transfer of precipitate to the filter paper. After the last washing by decantation, much of the precipitate still remains in the beaker. The loose part of this precipitate is transferred to the filter as shown in Fig. 8.13. One hand holds the beaker and rod, while the other hand manipulates the stream of wash water. If the nature of the wash solution permits, a plastic squeeze bottle (p. 138) is more convenient to use than the glass wash bottle.

After the loose part of the precipitate is removed, adhering particles are dislodged with a *rubber policeman* (Fig. 8.14) fixed to another clean glass rod. Any precipitate adhering to the original rod is also dislodged, and the rod is rinsed so that the washings fall into the beaker; the original

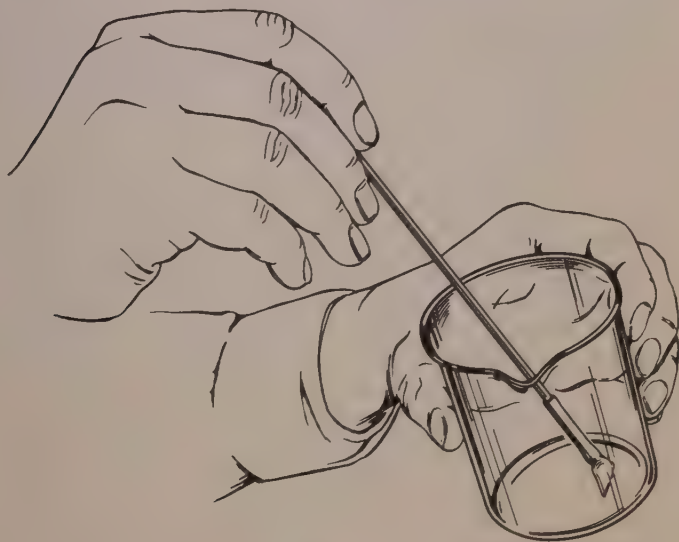


FIG. 8.14. Use of Stirring Rod with Rubber Policeman

rod is then laid aside. The dislodged precipitate is then transferred to the paper. The policeman should be wet with distilled water before contacting the precipitate. When a rod with a policeman is used for pouring, the beaker spout is placed against the policeman; if the spout is placed against the glass, solution may be lost as it flows over the shoulder of the policeman. The loosening and transfer process is repeated until inspection of the beaker shows no precipitate remaining.

Final washing of the precipitate on the filter. After the precipitate is quantitatively transferred to the paper, the final washing is begun immediately. A precipitate is never allowed to dry on the paper, nor even to drain for a long time, for it might cake or channel, and wash liquid would then drain ineffectively through the cracks.

If the washings need not be recovered quantitatively, it is expedient to substitute for the beaker that received the decantations a clean beaker to receive the washings, so that refiltration of a large volume will not be necessary if precipitate breaks through. To wash, the stream from the wash bottle is directed against the upper circumference of the paper, so that any precipitate there is carried into the vertex of the funnel. The jet is directed toward the bottom of the funnel, but should not strike the main body of precipitate hard or directly, or there may be loss by spattering. It is appropriate to start the stream well down from the edge of the paper, and then to bring it up to the edge, holding the stream stationary and rotating the funnel by the stem with the thumb and the index finger. The stream is kept longer on the three-thickness side of the paper than on the one-thickness side. When the paper is about half full of liquid, the stream is stopped and the water allowed to drain before another washing is made.

The number of washings depends upon the nature of the precipitate and the amount of washing done by decantation. To remove soluble impurities held with undrained mother liquor, three to four washings are needed. The number of washings may be counted by putting a mark for each washing on a piece of paper laid under the receiving beaker.

Test for completeness of washing. After an appropriate number of washings, the last portion is collected in a test tube and a reagent is added that gives a test (e.g., precipitate or color) for a substance originally present in the mother liquor, in order to ascertain that the latter is completely removed. For example, in the determination of chloride as AgCl , the mother liquor contains excess AgNO_3 . A test for complete removal of the excess Ag^+ may be obtained by adding a drop of HCl to the last wash portion and examining it for turbidity. Such tests must not be made too early, especially if the filtrate is to be recovered. Also, such tests are minimum ones. If the test is positive, washing is certainly not complete; but a negative test does not guarantee that strongly adsorbed or occluded impurities (or ones not tested for) have been removed.

Removal of the paper from the funnel. If it is dry, the paper comes out of the funnel easily, but there is danger of loss by flaking or dusting. Therefore it is preferable to remove the paper and the precipitate while still moist. The paper is loosened by prying the three-thickness side away from the glass with the tip of a clean spatula, then grasping the

paper and lifting it out. The fingers should never touch the inside of the paper. Any precipitate that has spattered onto the sides of the funnel may be wiped off with a quarter of clean, damp, ashless paper, which is then added to the main precipitate.

Miscellaneous comments on filtering and washing. (1) Whenever solubility and other properties permit, systems are filtered hot and washed with hot liquids. Hot liquids not only remove impurities more efficiently, but also filter faster than cold ones. (2) To prevent excessive loss by peptization or solubility, or to replace adsorbed impurities with less objectionable ones, washings are often made with solutions other than pure water. Solutions of salts, dilute acids, mixtures of alcohol and water, etc., may be used. A small wash bottle should be reserved for such solutions in addition to the regular wash bottle used for distilled water. (3) It is more efficient to wash with several small portions of wash liquid than with just one large portion. (4) Several filtrations may usually be carried on simultaneously, with little more effort than is required for one alone. However, order is necessary to prevent mix-ups. Each filter and receiving vessel should be marked to correspond to the beaker which contains the unfiltered system, and these should all be grouped closely together on the bench top.

8H.2. Filter Crucibles

Filter crucibles are generally recommended over filter papers. The uses and properties of several types are described in the following sections, with emphasis on those techniques not employed in paper filtration.

8H.2a. Sintered glass crucible. This is an all-glass crucible with a porous, sintered glass mat for the bottom. The nature of the precipitate determines which grade of porosity to use. Thus, Pyrex crucibles are made in three grades, coarse (C), medium (M), and fine (F). The crucible is very useful for heating precipitates below 500°C, at which temperature the glass begins to soften. Heating or cooling must be gradual, or the filter mat may crack.

8H.2b. Gooch crucible. This is a porcelain crucible with a perforated bottom (Fig. 8.15). A filter mat of asbestos fibers is laid down upon the bottom each time a filtration is made. (Using the same mat over again, by filtering a second precipitate onto one which has already been weighed from a previous determination, is not recommended.) Although more troublesome to use than the sintered glass crucible, it is still less trouble than filter paper. In contrast to the sintered glass crucible, it may be used for precipitates that must be ignited at high temperatures. It may also be used to filter many solutions that react with paper (e.g.,

permanganate, conc. HCl, etc.), or for precipitates that cannot be ignited with paper. Recently, glass-fiber filter disks have become available commercially in sizes that fit into the bottoms of standard per-

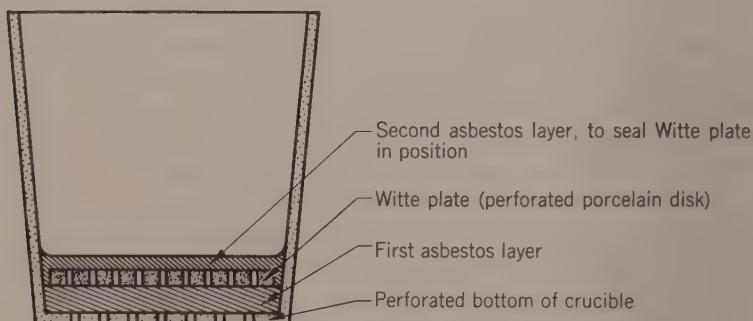


FIG. 8.15. Cross Section of the Gooch Crucible

forated crucibles. They are stable and retentive, yet fast. Easier to use than asbestos, they serve as well in many cases where high ignition temperatures are not required.

Preparation of the Gooch Crucible

1. Set up a clean, perforated crucible in the filter funnel, connected to the suction train as shown in Fig. 8.16.

2. With the screw clamp open and the aspirator shut off, fill the crucible with asbestos suspension, prepared by diluting the shelf reagent asbestos (Appendix IVD) about threefold with distilled water. Allow to stand for a minute or two in the crucible, until larger particles settle to the bottom, or until the liquid drains through.

3. To pack the mat, turn on the aspirator, and then close the screw clamp gradually until gentle suction is created. Too great a suction at this point may pull holes in the mat, in which case it should be removed and a new one laid down. The proper thickness of mat is about 1 mm; when the crucible is removed and held up to the light the perforations should be barely visible through the mat. In general, a thin mat is best, for the rate of filtration is a maximum. Once the mat is formed, liquid should never be added to the crucible except under suction, or the mat may be disrupted.

4. Place a clean Witte plate upon the mat, and pour in (under suction) just enough more of the asbestos suspension to seal the edges. Guide the flow of asbestos with a glass rod, so that it falls upon the edge of the plate rather than the center. The perforated plate protects the filter

mat from disruption when solutions are poured into the crucible. With care, the Witte plate may be omitted, giving more rapid filtration.

5. Pass several hundred milliliters of water through the mat, until the filtrate shows no sign of asbestos fibers. Then pass 500 ml more. When

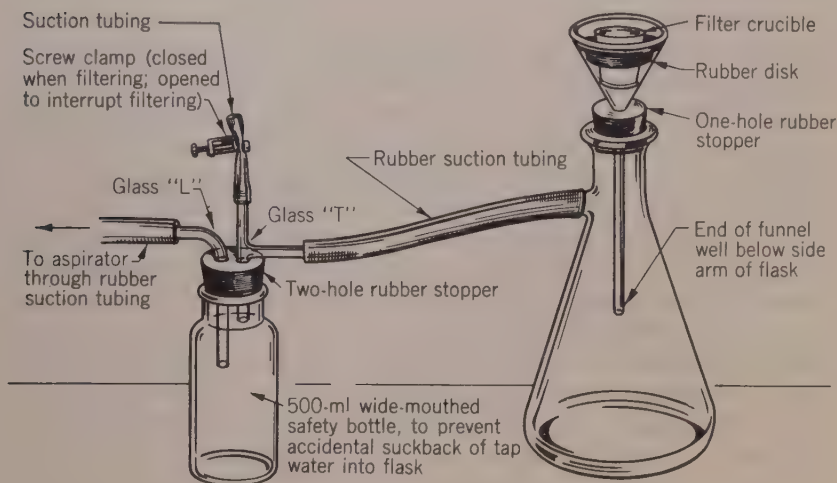


FIG. 8.16. Suction Train for Use with Filtering Crucibles

pouring solutions through the crucible, always pour down a glass rod, the lower end of which is held just above the surface of the solution in the crucible.

6. Remove the crucible, wipe the outside and bottom free of asbestos fibers with a clean cloth, and bring it to constant weight by the procedure intended for the precipitate. In being brought to constant weight, the crucible should be washed with several hundred milliliters of water between dryings and weighings, to ascertain that all loose asbestos is removed. To remove the crucible from the funnel, first open the screw clamp while the aspirator is still on. Then slowly turn off the aspirator. Failure to do this may cause tap water to be sucked back into the safety bottle (or into the filtrate if there is no safety bottle), and may loosen the mat by back pressure. A wet crucible should never be ignited at high temperature directly, or the mat may be disrupted. Instead, the crucible should be air-dried overnight, or heated for a short time in an electric oven at 100–150°C.

8H.2c. Other types of filter crucibles. Mats of materials other than glass or asbestos may be used in filter crucibles. *Porous porcelain crucibles* have sintered porcelain mats of various degrees of fineness, and may

be heated to 1200°C. Heating and cooling should be gradual, since the mat may crack. *Sintered quartz crucibles* may be used up to 1200°C, but they are very expensive. *Platinum filter crucibles* (Munroe crucibles) have porous platinum mats. The worker prepares the mat for each filtration by building up a layer of ammonium chloroplatinate in the bottom of a perforated platinum crucible, which is then ignited. Complete directions are given by Snelling (S22). Platinum is inert to some solutions that attack paper, porcelain, and glass (e.g., HF, conc. NaOH). Platinum crucibles have other advantages: they filter out very fine precipitates, yet filter rapidly; they attain constant weight rapidly because of the high heat conductivity of platinum; and they may be heated to considerably higher temperatures than porcelain crucibles. However, they are expensive, and are used only for very precise work. They may not be used for precipitates that attack platinum, or that reduce to metals alloying with platinum at high temperatures (e.g., sulfides, chlorides, Ag, Pb, etc.).

8H.2d. Stability of filter crucibles. No one type of crucible is better than another type for all chemical systems, but each type has its own unique advantages. Extended ignition or hard chemical treatment causes weight losses. The asbestos in Gooch crucibles is appreciably hygroscopic; after being removed from the desiccator and exposed to air, the crucible gains about 1 mg. Glass and porcelain crucibles are quite stable to hot or cold water, dilute acids, and NH_3 , but they may undergo weight losses of many milligrams when subjected to hot alkaline solutions. Platinum crucibles show evaporational losses at high temperatures. The stability of crucibles is excellently and quantitatively summarized, with references, by Kolthoff and Sandell (K18).

Whenever instability is suspected, it is well to determine its magnitude by a blank or a control. If the weight change is small, a correction may be suitable; but if it is large, a modification of the analytical method may be necessary.

8H.2e. Miscellaneous techniques in filtering through crucibles. Filtration through crucibles demands precautions and techniques similar to those for paper filters (pp. 120–25). Since the capacity of filter crucibles is small, considerable attention is required.

To obtain a portion of filtrate for testing, the filtration is interrupted and a test tube is inserted into the filter flask, so that the filtrate is delivered into the test tube. The filtration is then continued until a suitable amount of filtrate accumulates in the test tube, when filtration is again interrupted and the test tube is removed.

To clean a Gooch crucible the whole mat is removed, and any precipitate adhering to the porcelain is removed by gentle scraping under a stream of water. Holes filled with matter are picked out with a needle.

Any remaining precipitate is removed with a suitable solvent. For crucibles with permanent or semipermanent mats, the bulk of precipitate is removed by gentle scraping under a stream of water, and the remainder with a solvent. The proper solvent for a particular kind of precipitate is sometimes described with the directions for analysis. Swett gives solvents appropriate for removing many kinds of analytical precipitates from platinum crucibles, and some of these solvents are also suitable for porcelain or glass crucibles (S34). The cleaning of sintered glass and porcelain crucibles is described in a more recent reference (B29).

8H.3. Miscellaneous Filtrations

Filtrations are not always performed just to isolate the precipitate for weighing. Other purposes include (1) quantitatively recovering and redissolving the precipitate in the next step, (2) quantitatively recovering the filtrate, or (3) quantitatively recovering both precipitate and filtrate.

1. If the precipitate is simply to be quantitatively separated from the filtrate and recovered (say, in a beaker) for further processing, several simplifications in technique are possible, the chief one being that quantitative transfer of precipitate from the original beaker to the filter need not be made. Washing of the precipitate may be done largely by decantation until the beaker is free of mother liquor, but a policeman need not be used. The part of the precipitate on the paper is then transferred back to the original beaker (containing the washed but untransferred portion of the precipitate) by one of two methods.

If the precipitate is to be redissolved, and if the solvent is an efficient one, it may be poured over the filter in several small portions, with a short wait between portions to allow solvent action. The portions are caught in the beaker containing the untransferred part of the precipitate. When no more precipitate is visible on the paper, it is washed free of the solution of the precipitate, the washings also being recovered in the same beaker. If the solvent is only moderately efficient, or if its volume is limited, it may be necessary to pour the same portion repeatedly through the filter. Two beakers must then be used, one of which contains the untransferred part of the precipitate. When no more precipitate is visible on the filter, then the paper, the funnel, and the contents of one beaker are quantitatively rinsed into the remaining beaker. Dissolving a precipitate upon the filter is the most desirable method of transfer, since little of the filter paper goes through into the next step. In examining the paper for residual undissolved precipitate, special attention must be given to the folds. If the precipitate is to be redissolved on the filter, paper is preferred to crucibles, since filtrates are not convenient to handle under suction.

If the solvent is not an efficient one, it may be best to transfer the whole washed paper and precipitate into the beaker containing the untransferred part of the precipitate, and then to subject the whole to the process for dissolution in the next step. The paper should be opened and laid on the bottom of the beaker with the precipitate on top. The difficulty here is that the paper usually disintegrates to a bulky mass, which is troublesome to remove after dissolution. For such operations crucibles with permanent mats are preferred to paper.

2. If only the filtrate is to be quantitatively recovered, the procedure is very simple. The only vital precaution is that all washings must be added to the filtrate until the mother liquor is quantitatively recovered.

3. If both filtrate and precipitate must be quantitatively separated and recovered, the techniques and precautions of both preceding sections must be observed.

8I. EVAPORATION

The purposes of evaporation may be twofold: (1) to reduce the volume of a system, and/or (2) to remove an undesired volatile component.

TABLE 8.2*
CHEMICAL RESISTANCE OF PYREX† AND VYCOR‡

SOLUTION USED IN TREATMENT§	AVERAGE WEIGHT LOSS OF A 250-ML FLASK (mg)	
	Pyrex	Vycor
Water.....	0.2	0.1
H ₂ SO ₄ , 0.5 M.....	0.4	0.1
H ₂ SO ₄ , conc. Only 50 ml used.....	1.6	1.3
HCl, 6 M.....	2.2	0.4
HClO ₄ , conc. Only 50–100 ml used.....	0.1	
NaOH, 0.05 M.....	90	40
NaOH, 0.5 M.....	290	
Na ₂ CO ₃ , 0.25 M.....	80	
KOH, 0.5 M (in ethyl alcohol).....	90	
NH ₃ , conc. (8 days).....	0.6	
NaCl, 5%, in 0.001 M HCl.....	0.1	
NaCl, 5%, buffered pH 7.0 	6.9	1.4
NaCl, 5%, buffered pH 8.4 	10	7.4

* Data taken from E. Wichers, A. N. Finn, and W. S. Clabaugh, *Industrial and Engineering Chemistry, Analytical Edition*, 13, 419 (1941), Figs. 1, 2, and 3, with permission of the publisher.

† A borosilicate glass (about 80% SiO₂, 13% B₂O₃, 5% Na₂O and other metal oxides).

‡ A soft glass leached to remove most metal oxides, leaving over 95% SiO₂.

§ Consists of 200 ml of solution boiled in a covered 250-ml Erlenmeyer flask for 6 hours. Solution replenished to 200 ml with water at 3 hours.

|| KH₂PO₄-Na₂HPO₄ buffers.

81.1. Apparatus

Evaporations are usually carried out in wide-mouthed vessels, such as beakers, evaporating dishes, or crucibles. During evaporation appreciable amounts of the container material may dissolve. The rate of solution of glass increases rapidly with temperature and with the alkalinity of the solution being evaporated. Table 8.2 gives information on the amounts of materials dissolved from flasks boiled with various kinds of solutions (W13). Soft glasses generally go into solution even more rapidly than Pyrex. On the other hand, fused silica is less reactive than Vycor, especially with alkaline solutions.

Even Pyrex beakers should be avoided for evaporation prior to throwing down a precipitate for weighing, or in other instances where silica interferes. Porcelain can be used for such evaporations because of its lower rate of solution, but platinum should be used for highest accuracy. Hot, strongly alkaline solutions attack all siliceous materials, and even platinum. If possible, alkaline solutions should be neutralized and acidified slightly before evaporation.

81.2. Technique

The preferred procedure for aqueous solutions is evaporation on the community hot plate, below the boiling point, so that there is no loss by spray or spattering. This is slow, and must be arranged to occur overnight or while the worker busies himself with other tasks. Virtually

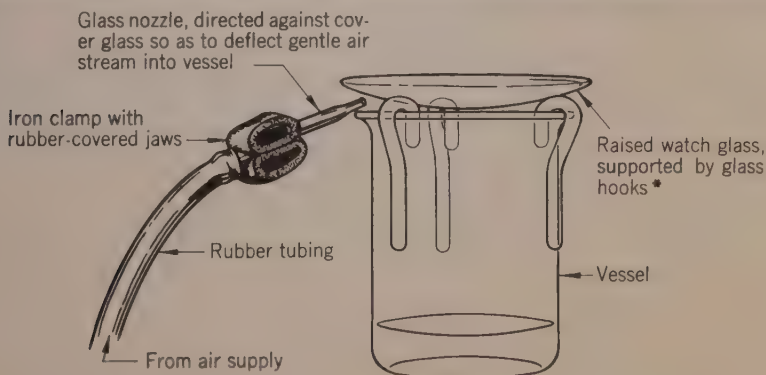


FIG. 8.17. Evaporation Hastened with an Air Stream

no attention is required from the worker. The vessel is covered with a raised watch glass, to prevent foreign matter from entering but still to allow the escape of vapors. The vessel should be not only wide-mouthed,

*Alternatively, a ribbed watch glass may be used without the glass hooks.

but also shallow, if possible, so that evaporation will be rapid. The rate of evaporation may be increased greatly with a gentle stream of air directed over the liquid surface, as shown in Fig. 8.17. All evaporations of noxious fumes must be carried out under the hood.

If the solution is boiled, the evaporation may be completed in a shorter time, but constant care and attention are essential. The vessel must be covered with a raised watch glass to prevent loss by spray or spattering. The vessel is best heated on a hot plate or in an air bath rather than by a direct flame, which heats unevenly and promotes bumping. Swirling or stirring subdues the violence of boiling.

As the evaporation proceeds, greater care must be exerted to prevent loss. The tendency toward loss by spattering, bumping, and decrepitation increases in the last stages, when the system becomes slushy, for then the heat distribution becomes poor and superheating occurs. The loss of a small amount of the concentrated residue may cause considerable error.

The extent of evaporation may vary. When only a reduction in volume is desired, the sides of the vessel should be kept clean. If any encrustation occurs, it must not be overheated, or it may be rendered insoluble. Some evaporations are conducted *almost to dryness*, that is, until only a moist residue is left; others may be carried *to dryness*, and the residue may actually be baked or heated after it is dry. The directions must always be studied to determine the extent of evaporation.

81.3. Bumping and Creeping

The difficulty with evaporation by boiling is that the system is liable to *bump*—that is, vapor bubbles may form with almost explosive violence, sometimes throwing the contents out of the vessel. Systems prone to bump should be evaporated below the boiling point, if possible. If this cannot be done, the following measures should be employed as far as practicable: (1) constant agitation or swirling, (2) a low rate of uniform heating, and (3) use of an air bath. The use of infrared heat virtually eliminates bumping, for the heat energy is applied to the liquid itself, where evaporation takes place, and not through a solid container wall that must be at a considerably higher temperature than the liquid for heat transfer to occur at a reasonable rate. The use of boiling chips or a capillary air leak is effective, but not often convenient, since quantitative recovery of the sought-for substance may be difficult.

Some liquids, especially those with high volatility or low surface tension, show a tendency to *creep* during evaporation. In creeping, the liquid wets the container walls far above the liquid surface; the liquid film may not only reach the top of the container, but may also go over the top and even down the outside, where it is lost.

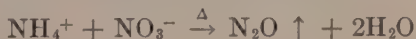
The creeping of aqueous solutions may be stopped by a band of collodion painted around the inside of the vessel, some distance above the liquid surface. However, this technique cannot be used with some solutions containing organic liquids or concentrated acids, which dissolve or destroy the collodion. Creeping may be greatly reduced by heating the vessel from the top rather than from the bottom. If the top walls of the container are kept hot, the liquid evaporates before it reaches the upper edge. The air bath helps to reduce creeping in this way.

8I.4. Removal of Acids and Ammonium Salts

It is sometimes necessary to eliminate an undesirable anion from solution. Nitrate, for example, interferes in the gravimetric determination of sulfate, and must be eliminated before BaSO_4 is precipitated. Nitrate may be destroyed by adding excess HCl and boiling. Likewise, chloride may be destroyed and replaced with nitrate by adding excess HNO_3 and boiling. Nitrate, chloride, acetate, and many other anions may be volatilized by being evaporated with concentrated, less volatile acids, such as H_2SO_4 or HClO_4 . The principal advantage of displacing a volatile acid in this way is that the solution need not be evaporated to dryness.

When a concentrated acid solution is evaporated, it should generally not be boiled, especially if the vessel is a small one, for these solutions have a tendency toward superheating, bumping, and creeping. Sometimes small volumes of liquids may be boiled without loss in large containers that are covered or have constricted mouths.

In some lengthy analyses, where repeated neutralizations are performed with NH_3 as the base, objectionably large amounts of ammonium salts may form and have to be eliminated. Ammonium salts are volatile and may be removed by evaporation to dryness and flaming at red heat. However, an easier method is to add an excess of HNO_3 (about 2 ml conc. HNO_3 per gram of NH_4Cl), and then to evaporate to dryness. Ammonium salts are volatilized by the reaction



8J. MARKING CONTAINERS

Identification of sample containers is extremely important in chemical analysis, where several determinations are often performed in parallel. Much effort may be lost when such identification is inadequate, for mix-ups may occur.

Most glass and porcelain vessels have small etched or unglazed areas that can be marked with a pencil; such areas, if not already present,

may easily be put on glassware with emery cloth. The pencil marks are removable with an ordinary eraser. Paper labels are generally unsatisfactory for marking glassware, except for reagent bottles. Labels wash off, scorch if heated, and cannot easily be brought to constant weight. Containers with paper labels should not be placed in drying ovens; reducing substances formed by decomposition of the paper and adhesive may react with the chemicals being dried.

For marking equipment that is to be heated much over 200°C , and that is to be accurately weighed, a permanent ink should be used. There are special porcelain-marking inks that fuse into the glaze upon ignition. Ordinary writing ink serves the same purpose, though the marks are not very intense. When such inks are used the crucible must be ignited to fuse the ink into the glaze, and then scoured and washed to remove excess ink before being brought to constant weight. Small pieces of equipment may be marked by filing small notches upon them. If a piece of equipment is in several parts, as a crucible and cover, each part should be separately marked. Metal containers may be marked by filing notches, scratching, or stamping.

8K. GLASSWORKING

Soft glass softens sufficiently for working at about 650°C , and may be worked with an ordinary Bunsen burner. Pyrex glass softens sufficiently for working at about 800°C , and must be worked with an oxygen-gas flame. All the equipment described in this section is constructed from soft glass.

8K.1. Glass Rod

To cut glass rod, a single, short scratch is made with a file where the break is wanted. Only one stroke of the file is needed, and this should be perpendicular to the axis of the rod. After being scratched, the rod is grasped firmly with one hand on each side of the scratch, the thumbs exerting slight pressure against the side of the tube opposite the scratch. The rod is held across the chest, with the scratched side down, and the hands are steadied on the chest, elbows out. To break the rod, pull it apart strongly with the hands, pressing lightly with the thumbs. A clean break should result. Moistening the scratch just before breaking is helpful. If the rod does not break, repeat the scratch. If the break is not clean, any small points remaining may be broken off by pressing them against the base of a burner, or by rubbing a wire screen lightly over them.

The newly cut end is delicate and razor-sharp. To prevent severe cuts, it should always be fire-polished. To *fire-polish*, the rod is held so

that the end just touches the blue inner cone of the burner flame, until the sharp edges begin to round off. The rod is rotated evenly, so that heating is uniform. Any degree of rounding may be obtained by varying the time of heating. If the rod is kept in the flame after rounding begins, a hemispherical end results; if it is kept even longer, a ball may be formed on the end of the rod. It is important to keep rotating the rod for some time after its removal from the flame, or the end may droop and cool in a bent position.

After its removal from the flame, glass must never be cooled rapidly, or weakening strains will develop. Hot glass should be laid upon the table edge or otherwise supported so that the hot part is in the air. Professional glass blowers *anneal* the hot glass, deliberately delaying its cooling by reintroducing it at brief intervals into the flame, by coating it with carbon from a sooty flame, or, best of all, by placing the glass in an annealing oven, the temperature of which is high enough for strains to work out but too low for softening to occur.



FIG. 8.18. How to Hold Glass Rod or Tubing for Heating—This mode of holding and rotating glass tubing may seem awkward to the student at first, but it is the correct way, since it permits easy transfer of the right-hand end to the mouth for blowing. Other simpler holding methods may be used if the tubing is not to be blown, but these are not recommended. The simpler methods are very difficult to unlearn later in the student's career when the work must be blown.

To *bend* glass rod, hold it in the flame as shown in Fig. 8.18. For bends over a short length of rod, the straight flame may be used, but for long bends the wing top should be employed. The glass is never bent in the flame; it is heated until it is sufficiently soft for working and

is then removed from the flame before being bent. Insufficient heating is a common mistake.

The important points to remember in working glass are: (1) Rotate continually to ensure uniform heating. (2) Synchronize the right- and left-hand motions to prevent twisting. (3) Keep both segments of the rod in a straight line, and do not let the glass bend or sag in the soft zone. (4) Do not push the segments together or pull them apart unless the thickness is to be changed. (5) Do all working out of the flame, which should be used only to soften the glass. (6) Ease, comfort, and relaxation are essential. Do not support a heavy or long piece in the hands alone; have a classmate help to support the long end, or improvise a support.

The most comfortable and efficient way to hold glass rod or tubing is shown in Fig. 8.18. Odd-shaped or unbalanced objects cannot always be held in this way. In such instances the method of holding and heating must be accommodated to the particular object, always with the precautions stated in the previous paragraph. The professional glass blower has many props and accessories (R12).

To construct *glass stirring rods*, cut soft glass rod (6 mm in diameter) into 15-cm lengths and fire-polish the ends. *Glass hooks* are made from glass rod (6 mm in diameter), to the dimensions of Fig. 8.19. The U-bend is made first, so that there is sufficient length of rod to grasp. Then the oblique bend is made. In making the bends the glass is heated in the flame until it is soft, and then removed for bending. Each bend should be examined from both the front and the side while cooling to make sure that the arms are at the correct angle and in the same plane. After the bend is cool, the short arm is cut to the desired length and fire-polished; then the long arm is cut and fire-polished.

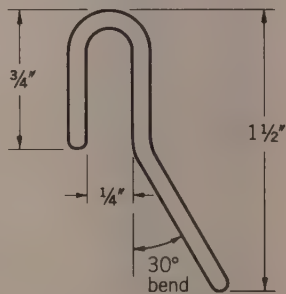


FIG. 8.19. A Glass Hook

8K.2. Glass Tubing

Cutting and fire-polishing are performed in the same way as for glass rod. In fire-polishing, the opening shrinks with heating, and may even be closed if heated long enough. Bending tubing is somewhat more difficult than bending rod; there is a tendency for tubing to collapse and/or kink if heated unevenly, insufficiently, or over too short a length.

To draw a pair of points, heat a segment of glass tubing in the straight flame, as shown in Fig. 8.18. When the tubing is soft, remove it from

the flame and pull it slowly apart, rotating it back and forth, maintaining tension and rotation until it is rigid. The resulting points should have the same axis as the original tube. The taper depends upon the length of tubing originally heated and upon the rate of pull. A *nozzle* may be made by cutting one of the points at whatever place gives a suitable diameter. In fire-polishing the nozzle tip, the thin-walled tubing closes very rapidly unless care is used. If thick nozzle walls are desired, the tubing should be pushed together somewhat during heating, so that the walls are thickened before the points are drawn.

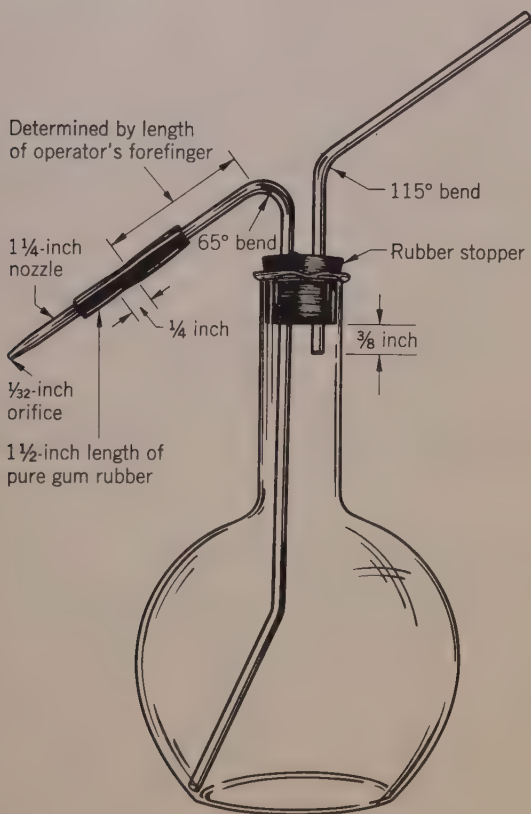


FIG. 8.20. The Wash Bottle

To *flange* the end of a tube, it is heated as for fire-polishing, and then turned against a hot file tip inserted slightly into the end of the tube, with the file axis inclined to the tube axis. The flange taper depends on the angle between the file and tube axis, and the flange length depends

on how far the file is pushed into the tube. Such flanges are useful in anchoring rubber tubing or bulbs onto the ends of glass tubing.

A pair of *droppers* may be prepared by drawing a 25-cm length of soft 6–8 mm glass tubing to points at its center. The points are cut off, fire-polished, and the large ends are flanged. Each dropper should be calibrated by scratching it lightly with a file at a position from which it delivers 1 ml when emptied. The number of drops per milliliter should also be determined, with the dropper held in a vertical position. (There should be 20–30 drops per milliliter.) In using droppers, the solution should not come in contact with the rubber bulb. If the bulb is accidentally wetted, it should be removed, rinsed, and allowed to dry before further use.

A *wash bottle* is shown in Fig. 8.20. The nozzle and mouthpiece are made as described previously. The long tube is most easily made by forming the upper bend first, then cutting to size, and fire-polishing both ends. After the tube is inserted in a two-holed rubber stopper, the lower bend is made so that the end of the tube comes to the edge of the flask bottom. To handle hot solutions, the neck of the flask should be wrapped with cord. To prevent blowback of steam into the mouth when hot solutions are used, a third hole may be bored through the stopper. To deliver a stream, this hole is covered with the thumb; to stop the stream, the thumb is raised an instant before blowing is stopped.

Squeeze bottles made from flexible *polyethylene* are very useful, and require no blowing to deliver liquid. These bottles have only an outlet nozzle, through which a stream of liquid is delivered by squeezing the bottle with the hand.

8K.3. Inserting Tubing in Rubber Stoppers

Probably the greatest number of minor but painful accidents in laboratories comes from attempts to insert glass tubing into stoppers. A lubricant (water, glycerol, or soap solution) should always be used. The tubing should be wrapped with a folded towel if convenient, should be grasped close to the stopper rather than far away, and should be inserted with a rotating motion and only slight pushing. As soon as the end of the tube emerges sufficiently to grasp, it should be pulled through the remainder of the way, rather than pushed. A safe way to insert glass tubing is first to insert a slightly larger cork borer into the hole; the glass tubing is then inserted through the borer, which is withdrawn, leaving the tubing in position.

After glass has been in a stopper for some time, it freezes or sticks to the rubber, and withdrawal is difficult. In such cases, it is best to take no chances with breakage and injury, but to cut the stopper away with

a razor blade. A single longitudinal cut along the side of the stopper, down to the glass, allows the stopper to be peeled away.

8L. COMMUNITY EQUIPMENT

It is simply not economically possible for each student to have his own ringstands, his own steam bath, his own spectrophotometer, etc. But such equipment is available to him if he shares its use, expense, and *maintenance*. In return for this great benefit, the student should be willing to sacrifice some of his sovereignty and to contribute to the maintenance, cleaning, and repair of this apparatus. It is suggested that:

1. All community equipment should be set free at the end of each working period. Ringstands, clamps, rings, and other special equipment should be returned to their proper places in the laboratory or stock room, so that they will be available to other classes using the laboratory. All oven and furnace space should be set free at the end of each working period. Articles left therein may be confiscated. Likewise, apparatus should not be left in the community hoods or hot plates any longer than necessary.

2. The individual student's desk top and balance should be cleaned after each working period, since students in other classes must use them. Unclean desks or balances should be reported to the instructor, and then cleaned.

3. Community equipment should always be left clean. Even if a student must use a piece of equipment that is not clean originally, he should first report its condition to the instructor, and should then set it in order. It is simply not workable to reason that he may leave it dirty because it was dirty originally; this attitude causes intolerable conditions, since everybody contributes to a mess, but nobody cleans it up.

4. Any defect or malfunction of community equipment should be immediately reported to the instructor, who will see to its repair. Much major damage begins as a small defect, and would not occur if the defect were repaired in time.

9 COMPUTATIONS OF GRAVIMETRIC ANALYSIS

9A. THE MOLE

A *mole* (i.e., gram molecular weight) of a substance is the number of grams of that substance that is numerically equal to its molecular weight.* To find the number of moles in a given number of grams of a substance:

$$\text{Number of moles} = \frac{\text{number of grams}}{\text{molecular weight}} \quad (9.1)$$

Thus a mole of HCl is 36.5 g. In 27.4 g there is $27.4/36.5$, or 0.751 mole. In 0.582 mole there are 0.582×36.5 , or 21.2 g.

The concept of the mole is essential to chemical arithmetic. The interconversion of moles and grams should be practiced until it becomes as familiar as the interconversion of dollars and cents.

The mole is a weight unit, the size of which is proportional to the molecular weight of the substance. Equal numbers of moles of various substances therefore contain equal numbers of molecules.†

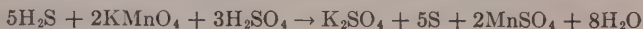
Atoms, ions, or molecules are the reacting units in a chemical reaction, and these react in the ratio of small whole numbers. Therefore the weights of reacting substances, expressed in moles, also stand in the ratio

*The term *molecular weight* is used loosely to represent the sum of the atomic weights in the formula of the substance, as written or understood from the context, no matter whether the substance is a molecule, ion, polymer, or a single atom. Thus a mole of H_2SO_4 is 98.08 g, a mole of sulfate (SO_4^{2-}) is 96.06 g, a mole of I is 126.90 g, and a mole of I_2 is 253.81 g.

†One mole contains 6.02×10^{23} molecules.

of small whole numbers. It is definitely advantageous to think in terms of moles as the reacting weight units, rather than grams, since the chemical arithmetic is greatly simplified. An illustrative example follows.

Example. Calculate the grams of S which could be produced by the action of 1.23 g KMnO_4 on excess H_2S in the presence of H_2SO_4 , according to the equation



Mole method:

2 moles of KMnO_4 yield 5 moles of S.

1 mole of KMnO_4 yields $5/2$ moles of S.

y moles of KMnO_4 yield $(5/2)y$ moles of S.

$$\frac{1.23}{158.04} \text{ mole of } \text{KMnO}_4 \text{ yields } \frac{5}{2} \times \frac{1.23}{158.04} \text{ mole of S, or } \frac{5}{2} \times \frac{1.23}{158.04} \times 32.064 = 0.624 \text{ g S.}$$

Gram method:

2×158.04 g KMnO_4 yield 5×32.064 g S.

1.23 g KMnO_4 yield z g S.

$$\frac{2 \times 158.04}{1.23} = \frac{5 \times 32.064}{z}$$

$$z = 1.23 \times \frac{5 \times 32.064}{2 \times 158.04} = 0.624 \text{ g S.}$$

The difference between the two methods of solving the example above lies in the way of thinking. In the mole method moles are pictured to be the reacting units, whereas in the gram method grams are pictured to be the reacting units. Although both methods are correct, the mole method is recommended in preparation for future work.

9B. GRAVIMETRIC CALCULATIONS

In the gravimetric determination of an element in a sample, the element can seldom be isolated and weighed directly; instead it is quantitatively converted to a pure compound of definite composition, which is then isolated and weighed. From the weight of compound, the weight of the element in the original sample is calculated. Since one atom of the sought-for element in the original sample yields one atom of that element in the final, weighable compound, it is not necessary to write detailed and balanced chemical equations for the conversion process, as shown in the following examples.

Example 1. An ore is treated with conc. HNO_3 and KClO_3 , to convert all S to sulfate. The nitrate and chlorate are then removed by repeated fuming with conc. HCl , and the sulfate is precipitated and weighed as BaSO_4 . What is the % S in an ore, 1.000 g of which yields 0.5562 g BaSO_4 ?

It is necessary only to know that each atom of S in the sample ends as one molecule of BaSO_4 .

1 mole of BaSO_4 comes from 1 mole of S.

$$\frac{0.5562}{233.40} \text{ mole of } \text{BaSO}_4 \text{ comes from } \frac{0.5562}{233.40} \text{ mole of S, or } \frac{0.5562}{233.40} \times 32.064 \text{ g S.}$$

$$\% \text{ S} = \frac{\text{wt. S}}{\text{wt. sample}} \times 100 = \frac{0.5562 \times 32.064 \times 100}{233.40 \times 1.000} = 7.64\% \text{ S}$$

Example 2. Cr in an ore exists as Cr_2O_3 , and is converted quantitatively to BaCrO_4 . Calculate the Cr content as $\% \text{Cr}_2\text{O}_3$, if a 0.500-g ore sample yields 0.2530 g BaCrO_4 .

1 mole of BaCrO_4 comes from $\frac{1}{2}$ mole of Cr_2O_3 .

$$\frac{0.2530}{253.33} \text{ mole of } \text{BaCrO}_4 \text{ comes from } \frac{1}{2} \times \frac{0.2530}{253.33} \text{ mole of } \text{Cr}_2\text{O}_3, \text{ or } \frac{1}{2} \times \frac{0.2530}{253.33} \times 151.99 \text{ g } \text{Cr}_2\text{O}_3.$$

$$\% \text{Cr}_2\text{O}_3 = \frac{\text{wt. } \text{Cr}_2\text{O}_3}{\text{wt. sample}} \times 100 = \frac{0.2530 \times 151.99 \times 100}{2 \times 253.33 \times 0.500} = 15.18\% \text{Cr}_2\text{O}_3$$

By now, most students have acquired their own methods of doing the arithmetic associated with chemical problems. In proceeding from one step to the next, some students prefer to use proportion; others prefer the dimensional (factor-label) method (**M16, S24**); and still others prefer the common-sense (reasoning) method.

It is possible to become so preoccupied with the arithmetical details of a problem that one loses sight of the chemical principles. In the illustrative examples of this text, an attempt is made to avert this danger by simply outlining the solutions. Particular methods are seldom advocated in proceeding arithmetically from step to step in solving the problem, and the student should provide his own method. In the outlines the intermediate steps are labeled, each label referring to the *whole* string of factors up to that label, starting from the left. Thus outline solutions* to the examples above are:

Example 1.

$$\frac{0.5562}{233.40} \times 32.064 \times \frac{100}{1.000} = 7.64\% \text{ S}$$

— moles BaSO_4 , or moles S — g S — % S

Example 2.

$$\frac{0.2530}{253.33} \times \frac{1}{2} \times 151.99 \times \frac{100}{0.500} = 15.18\% \text{Cr}_2\text{O}_3$$

moles BaCrO_4 — moles Cr_2O_3 — g Cr_2O_3 — % Cr_2O_3

*Ignore the dotted boxes until Sec. 9B.1 is read.

Unless a student definitely has other preferences, he should adopt this outline method of solving chemical problems; it is more compact and rapid than other stepwise procedures.

Even if the sought-for element does not appear in the final weighed product, the foregoing reasoning may be used, as shown in Ex. 3.

Example 3. A sample containing a mixture of alkali oxalates is analyzed for oxalate by precipitation as CaC_2O_4 . After being filtered and washed, the CaC_2O_4 is not determined as such, but is ignited to CaO and weighed. What is the % $\text{C}_2\text{O}_4^{2-}$ in a 1.2000-g sample that yields 0.2350 g CaO ?

1 mole of $\text{C}_2\text{O}_4^{2-}$ gives 1 mole of CaC_2O_4 , which in turn yields 1 mole of CaO .

$$\frac{0.2350}{56.08} \times 88.02 \times \frac{100}{1.2000} = 30.74\% \text{ C}_2\text{O}_4^{2-}$$

$\left[\begin{array}{c} \text{g C}_2\text{O}_4^{2-} \\ \text{moles CaO} = \text{moles C}_2\text{O}_4^{2-} \end{array} \right] \text{ g C}_2\text{O}_4^{2-} \text{ } \text{ \% C}_2\text{O}_4^{2-}$

9B.1. Gravimetric Factors

Each quantity enclosed within the dotted lines in the examples above is called a *gravimetric factor*, and represents the factor by which the weight of isolated precipitate must be multiplied to obtain the corresponding weight of sought-for substance in the sample. Thus

$$\left(\frac{\% \text{ of sought-for substance, } P}{P} \right) = \left(\frac{\text{wt. of precipitate obtained, } W}{\text{wt. of sought-for substance}} \right) \times \left(\frac{\text{gravimetric factor, } F}{F} \right) \times \left(\frac{100}{\text{wt. of sample, } S} \right)$$

$$P = \frac{WF}{S} \times 100 \quad (9.2)$$

For routine calculations, where the same factor is involved in many determinations, it is advisable to determine this factor (or its log) once and for all; it may then be used to obtain the weight of sought-for substance directly from the weight of precipitate in one step. This not only saves time, but also reduces the chances of error in computation. Some common gravimetric factors and their logs are given in chemical handbooks.

By proper selection of sample size for routine analysis, calculations may be practically eliminated, as shown in the Supplement (p. 670).

9B.2. Empirical Factors

The relationship between a sought-for substance and the weighed precipitate may not be strictly stoichiometrical—that is, a small, integral number of moles of sought-for substance may not give a small, integral

number of moles of the weighed product, owing to side reactions, incomplete reactions, or losses. In such a case, if the deviation from the stoichiometrical value is reproducible, an empirical factor may be used. For example, small amounts of phosphate may be determined as ammonium phosphomolybdate, $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$. According to the formula, this precipitate should contain 1.65% P, but experimentally it contains 1.63%. This experimental value may be used as an empirical factor in computing the weight of P in a given weight of the phosphomolybdate (K18).

If an empirical factor is found that is appreciably different from the theoretical, the existence of error is indicated. Such error may be highly dependent upon experimental conditions. When an empirical factor must be used for lack of a better method, the worker should first perform analyses on known samples, to make sure that the factor to be employed applies to the conditions of his analyses.

9C. REPORTING A QUANTITATIVE ANALYSIS

The manner in which the result of a quantitative analysis is reported depends in part upon the form in which the sought-for element exists in the sample, and in part upon the qualitative composition of the sample.

Frequently the form in which the sought-for element exists in the original sample is not known, or the element may be distributed among several compounds. Then the amount of that element may be reported as an amount (or percentage) of that element itself or, less desirably, as the oxide. There is then no commitment as to the form in which the element exists in the sample. This is the most definite method of reporting a result, but it is also the least informative. Thus the S content of an ore containing metallic sulfides may be reported as % S. Similarly, the Na content of a mineral may be reported as % Na, or % Na_2O , even though the element or its oxide is too reactive to exist as such in the atmosphere. This procedure is used in reporting analyses of complex materials such as minerals, glass, ceramics, and cement.

Occasionally the determined element is known to exist predominantly as a certain compound in the original sample. In such a case, the amount (or percentage) of that compound may be calculated and reported. If, for instance, a sample is known to contain KCl as the only chloride-containing compound, the result of a chloride analysis may be reported as a percentage of KCl. This method of reporting may sometimes yield percentages greater than 100%, which seems impossible unless properly interpreted. Thus if a sample containing only KCl and NaCl is analyzed for Cl, the Cl content as % KCl will be 100% or more (see Probs. 4 and 5, Sec. 9C, p. 148).

Reporting the percentage of a particular compound may be mislead-

ing or ambiguous if the percentage is inadequately labeled. For example, S in certain types of Cu-bearing ores may exist predominantly as CuS, and the S content may be reported as % CuS. But it does not suffice merely to report that the ore contains 20.0% CuS, for the reader cannot tell whether this represents an analysis for S or for Cu. In fact, an analysis of this ore for both S and Cu may be reported: Cu content, as CuS = 22.0%; S content, as CuS = 20.0%. These two percentages would be identical only if CuS were the only form in which both Cu and S exist in the ore (see Probs. 6 and 7, p. 149).

It is desirable, whenever possible, to report a constituent in a form that indicates its valence state in the original sample. For example, the result of a sulfate analysis may be reported as SO_3 , of a sulfite analysis as SO_2 , and of a sulfide analysis as S. It is also desirable to report the constituents of a sample in such forms that the percentages of all constituents add up to 100% in the original sample; however, this can be done only if the qualitative composition of the sample is known.

Occasionally results are reported in a way peculiar to the type of sample or the method of analysis. The convention used in such reports must be known and understood before the reports make sense. In different kinds of water analysis, for example, total hardness, carbonate, and calcium may all be reported as CaCO_3 , which may be extremely confusing to the uninitiated. Such methods are not used in the elementary analytical course.

9D. INDIRECT ANALYSIS OF MIXTURES

When one of two substances is difficult to separate and determine individually, it may be possible to determine the other substance directly, and also to determine the sum of the weights of both substances. The weight of the sought-for substance may then be found by difference, as shown in the following example.

Example. A 2.00-g sample of limestone gives 0.0971 g of combined oxides (Al_2O_3 and Fe_2O_3). By volumetric analysis of another sample of the same limestone, the % Fe_2O_3 is found to be 1.50%. What is the % Al_2O_3 ?

$$\begin{aligned} \left(\begin{array}{c} \% \text{ of combined oxides:} \\ \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 \end{array} \right) &= \frac{0.0971}{2.00} \times 100 = 4.86\% \\ \% \text{ Al}_2\text{O}_3 &= 4.86 - 1.50 = 3.36\% \end{aligned}$$

Any single constituent of a mixture may theoretically be determined by difference, if amounts of all other constituents are known. However, there are practical defects to this procedure. (1) If there are unrecognized constituents present, the result will be in error. If other oxides are present in the example above, the reported 3.36% Al_2O_3 is corre-

spondingly in error. It would be more correct to call the remaining 3.36% a percentage of residual oxides, rather than a percentage of Al_2O_3 . (2) In taking the difference between two quantities, there is a loss of precision. This loss is not great if a major constituent is determined by difference, but it is poor practice to determine a minor constituent by difference. In the example above, if there were 4.70% Fe_2O_3 , the % Al_2O_3 would be $4.86 - 4.70 = 0.16\%$. This small difference has a large relative uncertainty.

If it is at all possible to determine each constituent in a mixture, this should be done. The accuracy of the analysis may then be checked, since the percentages of all constituents should total 100. This check is sacrificed if one substance is determined by difference.

Even if neither of the two components can be directly found, it may still be possible to analyze the mixture indirectly, as shown in the Supplement (p. 671).

9E. REPORTING ANALYSES ON THE DRY BASIS

If an analysis is performed on a sample weighed out after drying, the result is automatically reported on a dry basis. Many analyses are made in this way. However, it is sometimes more convenient to make an analysis on an undried portion of a sample (as received), and to determine the moisture on another portion. The result may then be reported either on an *as-received basis* or on a *dry basis*, as the following example shows. Reasons for drying samples before analysis were given and drying techniques were described on page 103.

Example. A 2.000-g portion of a sample is dried to a constant weight of 1.975 g at 110°C . Analysis of another 1.000-g portion for chloride without drying gives 0.9525 g AgCl. Report the % Cl on an as-received basis, and also on a dry basis.

$$\frac{0.9525}{143.32} \times 35.453 \times \frac{100}{1.000} = 23.56\% \text{ Cl, as received}$$

\downarrow g Cl
 \downarrow moles of AgCl, or moles of Cl

$$\frac{2.000 - 1.975}{2.000} \times 100 = 1.25\% \text{ water, as received}$$

To calculate the % Cl on a dry basis, consider that 100 g of wet sample contain 23.56 g Cl and 1.25 g of water.

Hence 23.56 g Cl are contained in $100 - 1.25 = 98.75$ g of dry sample. The % Cl on a dry basis is therefore

$$\frac{23.56}{98.75} \times 100 = 23.86\% \text{ Cl, dry basis}$$

QUESTIONS

Sections 9B, C

1. A sample is a mixture of water-soluble alkali chlorides and sulfates. Give the various ways in which a gravimetric analysis for the sulfate content might be reported, indicating the most appropriate.

2. Give acceptable ways of reporting each of the following analyses, and give reasons in support of the way you think best.

(a) An ore for sulfides by gravimetric determination as BaSO_4 .

(b) A pure aqueous solution of CuSO_4 by gravimetric determination of sulfate as BaSO_4 .

(c) A CuSO_4 - K_2SO_4 mixture for sulfate by gravimetric determination as BaSO_4 .

(d) An iron ore by gravimetric determination of the Fe as Fe_2O_3 .

(e) A solution containing Na_2SiO_3 and Na_2SO_4 for Na, by conversion to NaCl , and weighing as such.

3. Interpret each of the following reports of analyses in as many reasonable ways as possible.

(a) 12.2% S

(b) 45.2% K_2SO_4

(c) 56.4% K_2O

(d) 21.9% SO_2

(e) 73.8% CuS

(f) 16.7% SO_3

(g) 34.7% Ag

(h) 34.7% Cl

(i) 37.4% AgCl

(j) Ag content, as AgCl , 37.4%

(k) Cl content, as AgCl , 37.4%

(l) SO_4 content, as CuSO_4 , 24.8%

(m) Cu content, as CuSO_4 , 24.8%

(n) 24.8% CuSO_4

(o) 81.9% Fe_2O_3

4. Give an example, other than that in the text, in which the sought-for substance does not appear in the final weighed product.

Section 9E

1. Why are samples usually dried before being weighed out for analysis?

2. Why are results of analyses usually reported on a dry basis, rather than an as-received basis?

3. Why is it important to describe the method of drying the sample in reporting an analysis? What constitutes such a description?

PROBLEMS

Section 9A

(Elementary problems in stoichiometry may be found in Sec. 4A, p. 34.)

1. How many grams are in 0.0657 mole of each of the following compounds: Fe_3O_4 , SnCl_2 , BaCO_3 , Hg_2Cl_2 , HClO_4 ? *Ans.* 12.98 g, for BaCO_3 .

2. How many moles are in 17.6 g of each of the compounds of Prob. 1?

Ans. 0.0893 mole, for BaCO_3 .

Section 9B

1. Give gravimetric factors for the following conversions: (a) Fe_2O_3 to Fe_3O_4 ; (b) AgCl to KClO_4 ; (c) BaSO_4 to $\text{Al}_2(\text{SO}_4)_3$; (d) $\text{Mg}_2\text{P}_2\text{O}_7$ to $\text{Ca}_3(\text{PO}_4)_2$; (e) Cu to Cu_3S ; (f) K_2PtCl_6 to K_2O . *Ans.* (d) 1.3936.

2. Calculate the factor for converting the weight of AgCl found in a gravimetric analysis to $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, which is assumed to be the only chloride-containing component in the sample.

3. A 0.2905-g sample containing only Pb_3O_4 and inert matter gives a precipitate of PbSO_4 weighing 0.3819 g. What is the purity of the sample? What is the % Pb?

Ans. 99.07%, 89.82%.

4. A 1.500-g sample contains $\text{K}_2\text{S}_2\text{O}_8$ as the only sulfur compound. After treatment to convert all S to sulfate, and precipitation of the latter as BaSO_4 , 1.675 g of BaSO_4 are obtained. Calculate the % $\text{K}_2\text{S}_2\text{O}_8$ in the sample.

5. How much AgNO_3 is required to precipitate all the chloride from a 2.000-g sample containing pure KCl, if a 10% excess is to be used? What volume of 0.500 M AgNO_3 would be required?

Ans. 5.013 g, 59.0 ml.

6. A sample of potassium alum, $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$, weighs 2.000 g. Quantitative precipitation of the Al and ignition to Al_2O_3 give a precipitate weighing 0.2125 g. (a) What is the percentage purity of the alum? (b) What is the % SO₃ in the alum? (c) What weight of BaSO_4 would the sample have given?

7. A 0.6235-g sample containing Mg gives 1.5913 g of the hydroxyquinolate, $\text{Mg}(\text{C}_9\text{H}_6\text{ON})_2$. What is the % Mg in the sample? What is the Mg content, as MgO ?

Ans. 19.848%, 32.91%.

8. A 1.100-g sample contains 60.00% NaCl and 40.00% KCl. What weight of AgNO_3 would be required to react stoichiometrically with the sample? What volume of 0.925 M AgNO_3 would be required?

9. A 1.200-g sample of an ore gives a precipitate of $\text{Mn}_2\text{P}_2\text{O}_7$ weighing 0.6000 g. What is the Mn content of the ore, as % MnCO_3 ?

Ans. 40.50%.

10. A 1.6345-g sample of a Ni alloy gives 0.3385 g of the oxinate, $\text{Ni}(\text{C}_4\text{H}_7\text{O}_2\text{N}_2)_2$. What is the % Ni?

11. A 1.5000-g sample of an ore is treated to recover Co as CoSO_4 , 0.1023 g being obtained. What is the Co content of the ore, as % CoS?

Ans. 4.004%.

12. A 1.000-g sample of a Bi alloy gives 0.1839 g BiOCl . What is the % Bi in the alloy?

13. How much MgO is required to give 0.900 g MgNH_4PO_4 ? *Ans.* 0.2642 g.

14. Sodium may be determined by precipitation and recovery as sodium zinc uranyl acetate hexahydrate, $\text{NaZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$. If a 1.000-g sample gives 0.308 g of precipitate, what is the % Na in the sample?

15. The arsenic in a 0.6270-g sample of an ore is oxidized to arsenate, which is precipitated to give 0.1693 g $\text{MgNH}_4\text{AsO}_4$. What is the As content of the ore, as % As_2O_3 ?

Ans. 14.73%.

16. What volume of conc. NH_3 (Appendix IVB) is required stoichiometrically to precipitate the Fe in 150 ml of a solution containing 0.100 M HCl and 0.850 g of ferric alum, $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$?

17. What volume of 0.1000 M $\text{K}_2\text{Cr}_2\text{O}_7$ solution must be taken to give 0.1863 g Cr_2O_3 after reduction, precipitation as the hydrous oxide, and ignition?

Ans. 12.26 ml.

Section 9C

1. A certain ore is reported to contain 7.82% As. What would be the As content as As_2O_3 ?

Ans. 10.33%.

2. An ore contains various copper oxides and sulfides. A 0.5000-g sample is treated to dissolve all Cu, which is then precipitated and ignited to CuO , giving 0.2886 g of the latter. Report the Cu content as Cu, Cu_2O , and Cu_2S .

3. The Fe content of an ore is reported as 56.58% Fe_2O_3 . What would be the Fe content, as Fe_3O_4 ? Fe? FeS_2 ?

Ans. 54.69% Fe_3O_4 .

4. A sample contains 86.0% NaCl. What is the Cl content, as KCl? As CaCl_2 ?

5. A sample may contain a high percentage of Na_2SO_4 , along with a small per-

centage of NaCl. Under the impression that the sulfate is K_2SO_4 , a worker reports the result of a sulfate analysis as 119.8% K_2SO_4 . Explain this result, and calculate the sulfate content as Na_2SO_4 .

Ans. 97.6% Na_2SO_4 .

6. A sample contains 35.0% $BaCO_3$ and 65.0% Na_2CO_3 . What is the Ba content, as $BaCO_3$? What is the CO_2 content, as $BaCO_3$? Explain the relationship of the two answers, and report the CO_2 content in a more appropriate manner.

7. A sample contains $CuSO_4$ and K_2SO_4 . A 1.700-g portion of this sample gives 0.1200 g Cu by electrodeposition. Another 1.700-g portion gives 0.5692 g $BaSO_4$ in gravimetric analysis. Compute the contents of Cu and of sulfate, each as % $CuSO_4$, and explain the relationship of the two answers.

Ans. 17.72%, 22.88%.

Section 9D

1. A mixture containing only Al_2O_3 and Fe_2O_3 weighs 1.0190 g. When the mixture is heated in a stream of hydrogen, the Al_2O_3 remains unchanged, and the Fe_2O_3 is reduced to Fe metal. A residue weighing 0.7744 g is obtained. What is the percentage composition of the original mixture?

Ans. 79.9% Fe_2O_3 , 20.1% Al_2O_3 .

2. What is the percentage composition of a brass sample containing only Cu, Zn, and Pb if a 2.000-g sample yields 0.0092 g $PbSO_4$ and 1.0765 g $Zn_2P_2O_7$?

Section 9E

1. An ore sample contains 2.03% moisture (as received) and 31.90% Fe (on a dry basis). What is the % Fe on an as-received basis?

Ans. 31.25%.

2. An ore sample contains 1.87% moisture and 42.68% Fe on an as-received basis. Compute the % Fe on a dry basis.

3. An ore sample contains 48.26% Fe on a dry basis and 47.12% Fe on an as-received basis. What is the percentage of moisture in the ore as received?

Ans. 2.36%.

4. A sample contains about 1% moisture and 30% K (both on an as-received basis). It is desired to analyze two portions, as received, one for moisture and the other for Cl, and then to compute the % Cl on a dry basis. (a) If a maximum relative error of 0.1% is desired for the Cl content, how precisely must the water content be determined? (b) Repeat the computation if the moisture content is about 10%.

5. A soil sample contains 5.2% moisture (as received) and 39.76% SiO_2 (as received). (a) What is the % SiO_2 on a dry basis? (b) What is the % SiO_2 after the sample has been dried to reduce the moisture content to 1.1%?

Ans. (a) 41.94%; (b) 41.48%.

10 ANALYSIS BY EVOLUTION.

DETERMINATION OF WATER

This chapter describes methods of analysis that depend upon the evolution of a sought-for substance as a gas. By measuring the reduction in weight of the sample, or the weight of substance evolved, the amount of sought-for substance may be found. Thus water may be determined by weighing the sample before and after heating to determine the loss in weight, or by collecting the evolved water in a suitable absorbent and finding the weight of water directly. Similarly, carbonates may be determined by the loss in weight on thermal decomposition, or by measurement of the CO_2 given off.

Such evolution methods have obvious limitations, but are excellent elementary determinations. The chemistry and techniques are simple but important. The necessity of removing moisture is met in almost all determinations, whenever samples must be dried.

10A. HOW WATER IS HELD IN SOLIDS

Water may be conceived to be held in essentially two different ways in solids—physically and chemically. The several different mechanisms by which water may be held in a sample are classified below. However, this simple classification needs two qualifications.

1. All of the water in a particular sample is not necessarily bound by a single mechanism. In many cases, the bulk of the water may be bound in one way, but some of it may be bound in other ways as well. For instance, Ca(OH)_2 may contain adsorbed water as well as its water

of constitution. Hydrates may also contain adsorbed water in addition to their water of hydration.

2. Modes of water retention other than those listed are occasionally encountered, and the classification given below is not complete (B4).

10A.1. Physically Bound Water

Expulsion of physically bound water requires heat comparable to that required to evaporate water. Relatively gentle heating at 100–105°C (or just exposure to a dry atmosphere) often suffices to remove the major proportion of physically bound water. The amount held is variable, and depends greatly upon the way in which the solid is formed and/or the conditions of temperature and pressure under which the solid exists. Water may be physically bound to a solid in several ways.

Dissolved water may exist within a solid, just as a dissolved solid may exist in a solution. At equilibrium such a solid solution is homogeneous, and exerts a water-vapor pressure that increases with temperature and water content. Even at elevated temperatures, drying may be slow because of the low rate of diffusion of water out of the solid.

Occluded water may be held within cavities in a solid, or may be adsorbed on the solid during growth and then covered over. Such systems are nonhomogeneous, the water being unevenly distributed. The amount of occluded water varies with the mode of formation and the treatment of the solid after formation. Occluded water may not always be removed at an appreciable rate by heating at 100°C, because of the low rate of diffusion of the water out of the solid. However, occluded water may be driven off at a finite rate at a sufficiently high temperature. For some solids that are impervious to water, exceedingly high temperatures may be necessary to eliminate occluded water in a reasonable time. BaSO₄ is such a substance.

Most solids precipitated from aqueous media contain occluded water. If relatively large amounts of water are held within cavities, the solid may decrepitate or shatter on being heated, owing to the high pressures formed when the water volatilizes to steam within the cavities; NaCl crystals tend to hold water in this way.

Surface-adsorbed water is held by adsorption upon the surface of the solid. Water so held exerts a vapor pressure, which increases with temperature, and is in equilibrium with the surroundings, thus:



The amount of adsorbed water increases with the water-vapor pressure of the ambient atmosphere (see Supplement, p. 682), and decreases with increasing temperature. Some finely divided substances that have great

surface area may hold rather large amounts of water in this way. The ease with which adsorbed water may be driven off varies greatly with the nature of the adsorbent. Water may be removed quite easily from some adsorbents, but may be removable only with difficulty from other adsorbents that have a great affinity for water.

10A.2. Chemically Bound Water

Water bound in chemical combination is held in a definite proportion by weight within the solid. Relatively larger amounts of energy are usually required to decompose such compounds and to drive off the water than are required for physically bound water.

Water of crystallization or water of hydration is molecularly bonded to the molecules or ions of the solid. Such water retains its identity as water within the solid. Examples are the hydrated salts: $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, etc. The properties of hydrates are described in the Supplement (p. 678); they are highly pertinent to analytical chemistry, being involved not only in the determination of water, but also in drying and desiccants.

Water of constitution is not present as water molecules within the solid, but as H and O atoms atomically bonded to other atoms of the solid. When the solid is decomposed, however, the H and O atoms form water, which is liberated. Fairly high temperatures are sometimes necessary to decompose such compounds (see Supplement, p. 676), among which are inorganic hydroxides like $\text{Ca}(\text{OH})_2$. Another example is NaHCO_3 , which decomposes at rather low temperatures.



10B. THE DETERMINATION OF WATER

One of the most common of all analyses is the determination of water. Water is used in the preparation of many materials, and remains in them as a combined constituent, contaminant, or diluent. Some materials also pick up moisture from the air. A knowledge of the amount of water in samples is usually important, and is often required along with information on the amounts of other substances.

Water determination is often complicated by the fact that it may be held in so many different ways in the sample. If the problem is to find the total water content of the sample as received, the answer is fairly simple: heat to drive off all water, and determine the evolved water by loss in weight or by absorption. All too often, however, the problem is to determine only a particular kind of water in the sample, and this may

lead to complications. For example, in analyzing a mixture of NaHCO_3 and Na_2CO_3 , it might be desired to find the NaHCO_3 content by the loss in weight on heating to 300°C , according to Eq. 10.2. The difficulty is that the sample may contain other water (adsorbed on the solids, or water of hydration of the Na_2CO_3). There will be error if this other water is not removed before carrying out the decomposition. This other water cannot be removed simply by drying the sample at 105°C , because NaHCO_3 begins to decompose even at so low a temperature. Therefore the slower process of drying at room temperature in a desiccator is necessary. In many cases the problem cannot be so simply solved.

The direct and indirect determination of water is described in the two following sections. Additional instructive methods are described in the Supplement (p. 688).

10B.1. Indirect Determination by Oven-Drying

The sample is heated at a temperature sufficient to drive off the water, and the loss in weight is taken as a measure of the water content of the

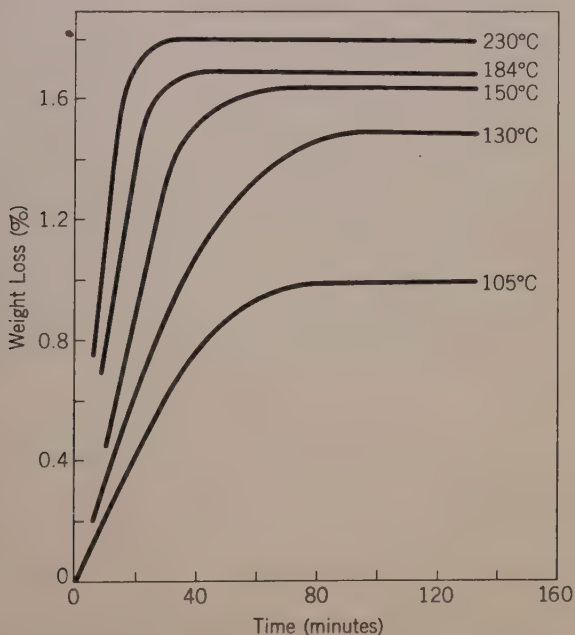


FIG. 10.1. Oven-Drying of an Organic Sample in Air (Reprinted from C. O. Willits, *Analytical Chemistry*, 23, 1058 [1951], Fig. 1, by permission of the publisher.)

original sample. The principal advantage of this method is simplicity. The disadvantage is that any other weight changes that occur on heating cause error. Such changes may be brought about by (1) volatilization of other components than water, such as other solvents and oils, (2) loss of water of constitution (especially with organic compounds), or (3) oxidation or decomposition of the sample. Another disadvantage of the oven-drying procedure is that some samples form crusts impervious to moisture, stopping evaporation before all moisture is removed. Molasses, cereals, and plant or animal tissues sometimes behave in this way.

Many inorganic mixtures may be dried to constant weight over a range of temperatures, as in the drying of hydrates of stable substances. In such cases the loss in weight may be assigned a definite meaning. But such behavior must always be established before the loss in weight can be accepted as being due solely to water. Not all samples behave so simply.

Figure 10.1 shows curves for the loss in weight of an organic sample dried at various temperatures (W17). It may be seen that a fairly constant weight is soon reached at each temperature, but that the total loss in weight when constancy is reached depends upon the temperature of drying. This behavior is typical of many substances containing water. Any "water content" based on such a loss in weight is therefore rather arbitrary, so the drying conditions must be carefully stated and must accompany any reported value.

In general, oven-drying is carried out at the lowest practical temperature, in order to minimize decomposition. However, the rate of drying decreases with decreasing temperature, and sets a lower limit to the temperature that may be employed. Sweeping with a dry gas stream or drying in a vacuum oven sometimes increases the rate of drying at lower temperatures. Samples unstable to heat may be dried at room temperature in a desiccator or vacuum desiccator.

10B.2. Direct Determination by Absorption

Here, the sample is decomposed and the evolved water is determined after its absorption in a reagent specific for water. This procedure avoids many of the difficulties of the oven-drying method, such as errors due to volatilization of solvents or components other than water. But it is still unable to distinguish between water held as such by the sample and water formed by decomposition or oxidation. Generally, the absorption method is used only to determine the total water content. The absorption method is among those used to measure the vapor pressure of hydrates and the moisture content of silicate rocks.

10C. OTHER EVOLUTION METHODS OF ANALYSIS

The CO_2 in a sample of decomposable carbonates may be driven off by heating, the difference in sample weight before and after heating being taken as the CO_2 content. (The decomposition process is described in more detail in the Supplement, p. 690.) In this method, CO_2 is assumed to be the only volatile substance in the sample, and the limitations are similar to those involved in the indirect method for water. In a few applications, such as the determination of CO_2 in limestones, the indirect method is simple and useful. Because so little manipulation is needed, the method is also amenable to the indirect analysis of simple mixtures (p. 671).

The interferences in the indirect method may be overcome by directly measuring the CO_2 evolved instead of the weight loss of the sample. To do this, the sample is decomposed in a stream of CO_2 -free air. The air stream is then passed through an absorbent that removes CO_2 ; the increase in weight of the absorbent gives the weight of CO_2 . Unlike the indirect method, change in weight of sample due to reaction of other constituents causes no error. If volatile and absorbable products other than CO_2 are formed, they must be removed from the air stream before it reaches the absorbent.

CO_2 and H_2O may be determined directly in a sample that gives off H_2O upon decomposition as well as CO_2 . The effluent air stream is passed first through a tube containing Anhydrone (anhydrous $\text{Mg}(\text{ClO}_4)_2$) which removes H_2O but passes CO_2 . The stream is then passed through a tube containing Ascarite (asbestos impregnated with NaOH) to remove CO_2 . The gain in weight of the Anhydrone tube represents the water evolved by the sample, whereas the gain of the Ascarite tube represents the CO_2 evolved. This procedure is used in the analysis of organic compounds by combustion for H (giving H_2O) and C (giving CO_2). Many important details necessary for adequate accuracy are omitted in this brief description (F11).

Carbon in steel may be determined by burning the steel in a CO_2 -free stream of oxygen and passing the effluent gas stream through an absorbent for CO_2 (S9). In some methods the evolved CO_2 is collected as a gas, and the volume measured instead of the weight (S11).

There are other evolution methods of analysis, some of which are outlined in the Supplement (p. 690). However, the classical evolution methods, in which the sample is simply heated to the decomposition temperature, have always been of rather limited application. Generally, the decomposition of compounds under such uncontrolled conditions is not stoichiometrical enough for quantitative analysis. Also, by classical

methods, thermal decomposition is not very selective—that is, if a mixture is heated sufficiently to decompose the sought-for compound completely, other constituents may also be partially decomposed.

Within the past decade, however, the thermobalance (see Supplement, p. 692) has brought a high degree of control to the evolution method of analysis. Accuracies and procedures are now feasible that were previously unachievable by classical evolution methods.

EXPERIMENT 10.1. INDIRECT DETERMINATION OF WATER

The water content of a $\text{NaCl-BaCl}_2 \cdot 2\text{H}_2\text{O}$ sample is determined indirectly from the weight loss on heating.

PROCEDURE

For techniques, read the introduction to Chapter 8 (p. 96).

1. Prepare two small weighing bottles. (a) If the weighing bottles and stoppers do not have identifying marks, mark them. (b) Put both weighing bottles and stoppers in a 250-ml beaker and rinse with cleaning solution, then with tap water, and then with distilled water. Dry the weighing bottles, stoppers, and the beaker with a clean towel. (c) Set each weighing bottle and its stopper in the 250-ml beaker, and cover with a raised watch glass (Fig. 8.1, p. 100). Heat for 1–2 hours in the electric oven at 150–160°C. (Note 1.) (d) Remove the beaker from the oven, place the weighing bottles while still hot into the desiccator, and slide the stoppers *loosely* into place. Permit the bottles to cool for one hour, and then weigh each bottle with its stopper to the nearest 0.1 mg. (e) Repeat steps c and d until two consecutive weighings agree within 0.2 mg. (Note 2.)

2. Weigh out 1–2 g of sample (Note 3) to the nearest 0.1 mg into each weighed bottle. (Notes 4, 5.)

3. Heat the sample to constant weight, as in steps 1c, d, e.

4. Report the % water in the sample:

$$\frac{\text{Weight loss, g}}{\text{Weight sample, g}} \times 100 \quad (\text{Note 6})$$

NOTES

(1) The bottle is brought to constant weight under the conditions anticipated for the sample. The dihydrate has a decomposition pressure that exceeds one atmosphere at a temperature somewhat over 100°C. Evolution of water proceeds at a good rate at 150°C. At 250–300°C, 20 minutes is sufficient for complete decomposition, but this requires a good electric oven, an electric furnace, or an air bath.

(2) If constant weight is not achieved within two weighings, consult the instructor.

(3) The recommended sample size is for a series of $\text{NaCl}\cdot\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ samples ranging from 90–100% $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$. Preparation of the series is described in the Supplement (p. 694). If a different series is used, the instructor will announce the appropriate sample size. Alternatively, unknowns may be dispensed with, and students may analyze reagent-grade $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$, which has a water content very close to the theoretical (14.75%).

(4) The sample is best weighed into the empty bottle right after the last weighing is made on the empty bottle. The direct method of weighing may be used, since the sample is stable in air.

(5) The dihydrate is stable in air over a moderate range of temperature and relative humidity (see Supplement, p. 679), so that no special precautions need be used in handling the sample. After heating, of course, the anhydrous BaCl_2 could remove water from the desiccant and from the air, but the good closure on the weighing bottle prevents this.

(6) The range of duplicate determinations should be less than 0.05% H_2O for excellent work. An example of a summary data page is shown below. This page should be made out before the experiment is begun, leaving spaces for the data, and should be filled in as the determination progresses.

SUMMARY DATA PAGE

EXP. 10.1. DETERMINATION OF WATER IN BaCl_2

Date begun

John Brown

Date completed

Locker No.....

Determination	I	II
Bottle no.	51	67
Wt. empty bottle, g		
1 heating (p. 1)	18.2634	19.7932
2 heatings (p. 1)	18.2635	19.7930
3 heatings		
Wt. bottle + sample, g (p. 2)	19.3924	21.1876
Wt. sample, g	1.1289	1.3946
Wt. bottle + residue, g		
1 heating (p. 3)	19.2266	20.9820
2 heatings (p. 4)	19.2262	20.9822
3 heatings (p. 4)	19.2263	
Wt. loss, g	0.1661	0.2054
% water (p. 5)	14.71	14.73
Average % water		
		14.72
Range, % water		0.02
Range, relative, p.p.t.		1

QUESTIONS AND PROBLEMS

Sections 10A, B

1. Why are samples usually dried before analysis?
2. Describe briefly how to find the water content of the following materials: (a) a sample containing Na_2SO_4 and K_2SO_4 ; (b) a silicate rock; (c) concentrated H_2SO_4 ; (d) plant leaves; (e) polished rice; (f) a cooking oil; (g) tank nitrogen.
3. Describe the process of drying the materials of Ques. 2 prior to analysis for other constituents. It is not necessary to determine the water content. For which of these materials might such drying not be very informative, and, in fact, even cause trouble?
4. Speculate on how water might be held by a sample to give the curves of Fig. 10.1 (p. 153).
5. In determining C and H in an organic compound by combustion, how should the influent air stream be treated to avoid error?
6. Explain why a small percentage of C in a steel sample cannot be determined by burning the sample in air and measuring the weight loss.
7. An organic sample weighing 0.7312 g is burned in oxygen, and the weight of water formed is 0.0912 g. What is the % H in the sample? *Ans.* 1.396%.
8. A 2.000-g sample containing only NaHCO_3 and Na_2CO_3 loses 0.2456 g when heated to 300°C , at which temperature decomposition of NaHCO_3 is complete, according to Eq. 10.2 (p. 152). What is the % Na_2CO_3 in the mixture?
9. A 2.000-g sample containing only Na_2CO_3 , NaHCO_3 , and water loses 0.7075 g when heated to 300°C , at which temperature all water is driven off and decomposition of NaHCO_3 is complete. The heating takes place in a stream of dry air that is passed through a tube containing Anhydrone. If the tube gains 0.3339 g, what is the composition of the original sample?
Ans. 9.05% water, 71.32% NaHCO_3 , 19.63% Na_2CO_3 .
10. (a) Hydrogen is determined in an organic compound by combustion in a stream of oxygen. Calculate the % H from the following data: weight of sample, 0.1730 g; weight of empty tube for absorbing water, 48.6532 g; weight of absorbent tube with water, 48.8074 g. (b) In taking the preceding data, the empty absorbent tube is inadvertently weighed full of air, whereas after combustion the tube is filled with oxygen. Estimate the error of the analysis, if the free volume inside the tube is 25 ml, and if the weighings are made at 25°C and 754 mm pressure. (c) How might the data be taken to avoid this error?
11. A 6.5-l sample of air at 16°C and 745 mm pressure is aspirated through a weighed Anhydrone tube, which selectively removes water. If the tube gains 120.5 mg in weight, what is the partial pressure of water vapor in the sample?
Ans. 18.5 mm.
12. Moisture in organic liquids was formerly determined by reacting the liquid sample with calcium carbide and measuring the volume of acetylene evolved:



If a 1.500-g sample gives 23.4 ml of acetylene at standard conditions, what is the % H_2O in the sample?

13. A 1.531-g sample of a hydrate of copper sulfate lost 0.5463 g when heated to constant weight at 150°C , which temperature is sufficient to drive off all water. What is the formula of the hydrate? *Ans.* $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

Section 10C

1. Devise and outline a procedure based on a chemical reaction for measuring the oxygen content of air.

2. A sample contains between 15 and 25% CaCO_3 . How much sample should be used for a CO_2 analysis so that a weight loss of at least 0.20 g is obtained?

3. A 0.843-g sample of limestone previously dried at 105°C gives a weight loss of 0.1345 g. What is the CO_2 content of the sample, as % CaCO_3 ?

Ans. 36.28%.

4. A 2.000-g sample of steel, when analyzed for C by combustion, gives 40.0 mg CO_2 . What is the % C in the steel?

5. A 1.000-g sample of limestone is dried to a constant weight of 0.9902 g at 105°C . On ignition to 950°C , the dried sample loses 0.450 g. (a) Assuming that only CO_2 is given off in the ignition, calculate the % CaCO_3 in the dried sample. Give possible explanations for this result. (b) What is the % CaCO_3 in the as-received sample? (c) What is the % H_2O in the as-received sample?

Ans. (a) 103.4%; (b) 102.3%; (c) 0.98%.

6. An organic compound may contain C, H, and O. Combustion of 0.1085 g of the pure compound gives 0.3411 g CO_2 and 0.1394 g water. Calculate the percentage composition and simplest formula of the compound.

7. Combustion of 0.1868 g of a pure organic compound containing C, H, Br, and possibly O, gives 0.2000 g CO_2 and 0.0955 g water. Conversion of all the Br in a 0.1550-g sample to AgBr gives 0.2369 g of the latter. Find the simplest formula of the compound. What additional information is needed to find the molecular formula of the compound?

Ans. $\text{C}_3\text{H}_7\text{Br}$.

Experiment 10.1

1. How might water be held in reagent-grade $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ to cause its water content to deviate slightly from the theoretical value?

2. Explain the effect of each of the following mistakes on the result of Exp. 10.1, and give the sign of the error, if any. (a) The original weighing bottle into which the sample is put is not completely dry. (b) The sample is erroneously dried at 105°C for an hour before weighing it out. (c) In obtaining the weight of sample and container before heating, a 50-mg fractional weight is incorrectly read as 20 mg. (Why is an error of this sort less likely to occur in obtaining the weight of the empty bottle, or of the bottle plus residue after heating?) (d) All weighing data are correct, but an arithmetical error is made in the subtraction to find the sample weight, giving 1.0289 g instead of the correct value of 1.1289 g. (e) Moisture is reabsorbed by the anhydrous BaCl_2 before weighing. (How might this be discovered?)

3. If the $\text{NaCl} \cdot \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ samples contain 90–100% of the dihydrate, what is the range of water contents of the samples?

Ans. 13.27–14.75%.

4. A sample contains 20–50% water. What is the minimum sample size that should be used to give a weight loss of at least 0.40 g on indirect analysis?

5. A 1.6830-g sample of $\text{NaCl} \cdot \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ gives a weight loss of 0.2479 g on heating. Calculate the % H_2O and the per cent of dihydrate in the sample.

Ans. 14.73% H_2O ; 99.9% dihydrate.

11 SOLUBILITY AND SOLUBILITY PRODUCT

11A. SOLUBILITY OF SOLIDS IN LIQUIDS

The solubility of a solute is defined as the quantity of solute dissolved in a unit volume of saturated solution. There are many units in which solubility may be expressed, but the important ones for the analytical chemist are molarity, normality, grams per liter, and weight percentage. These terms should be clearly understood before this chapter is studied.

The following paragraphs discuss the mechanism of the solution process and the factors upon which solubility depends, with particular emphasis on the solubility of electrolytes in aqueous media.

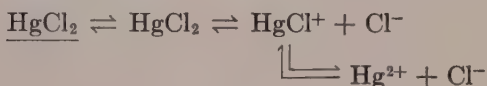
11A.1. The Solution Process

The molecules or ions of a solid exert attractive forces upon each other—forces that preserve the crystal structure and form of the solid. When the solid is immersed in a solvent, the solvent molecules also attract the surface molecules of the solid, and this attraction competes with the forces between solute molecules. If the solute molecules are attracted less strongly among themselves than by the solvent molecules, the attractive forces holding the solid solute together are overcome; the surface molecules then go into solution and the solid disintegrates or dissolves. This process continues until the solvent assimilates as much solute as it can hold, whereupon a state of equilibrium is reached.



This is a dynamic equilibrium, and it obeys the same laws as other equilibria.

Many inorganic compounds are electrolytes, that is, they go into solution as positive and negative ions, as well as in the form of molecules of the compound. Furthermore, these dissolved ions or molecules are hydrated. Thus a strong electrolyte like Na_2SO_4 exists in solution as sodium ions $(\text{Na} \cdot x\text{H}_2\text{O})^+$ and as sulfate ions $(\text{SO}_4 \cdot y\text{H}_2\text{O})^-$, which are quite independent of each other and are unassociated in the solution. On the other hand, a weak electrolyte like HgCl_2 exists predominantly in solution as hydrated HgCl_2 molecules $(\text{HgCl}_2 \cdot z\text{H}_2\text{O})$. Only a portion of the dissolved HgCl_2 exists as hydrated ions. The chemical equations for these dissolution processes are:



11A.2. Factors Influencing Solubility

Nature of solute. The preceding mechanism does not explain why some compounds are soluble and why others that are merely different combinations of the same kinds of ions are insoluble. Thus AgNO_3 , K_2SO_4 , and BaCl_2 are soluble, but AgCl and BaSO_4 are not. The attractive forces among ions and molecules are highly specific, and it is difficult to generalize about solubility. The solubility rules given in Table 4.1 (p. 22) are restricted empirical generalizations, and they should be memorized by the student. More comprehensive rules are not available at this time.

Nature of solvent. Compounds that are soluble and highly ionized in water may not be so in another solvent. Generally, inorganic salts are less soluble in organic liquids than in water. In a mixture of two solvents the solubility of a salt often, but not always, lies between its solubilities in the pure solvents.

The decreased solubility of salts in organic liquids is utilized in many ways in analytical chemistry. For example, Sr is often determined gravimetrically as SrSO_4 , which is only moderately insoluble in water, but quite insoluble in alcohol. Solubility losses are reduced by precipitating and washing this compound in an alcohol-water medium. However, it should be pointed out that in practice the solubility of a sought-for substance may not be reduced indiscriminately by this method, for the solubilities of other electrolytes present as impurities may also be reduced correspondingly, and contamination may increase.

Along similar lines, Na and K are separated before Na is determined by taking advantage of the relative insolubility of KClO_4 as compared to NaClO_4 in alcohol or ethyl acetate. As another example, FeCl_3 is quite extractable from an aqueous HCl solution into ether or other organic liquids not miscible with water, and Fe may be separated from many other metals whose chlorides are not so extractable. Solvent extraction is being used increasingly as a separation process.

Temperature. For most substances, the heat required to pull the solute molecules apart is greater than the heat evolved by solvation of the solute, and heat is absorbed in the solution process (i.e., in going from left to right in Eq. 11.1). According to Le Châtelier's principle, the solubility of such substances increases with temperature. For some substances, like NaCl , these two heat effects are pretty well balanced,

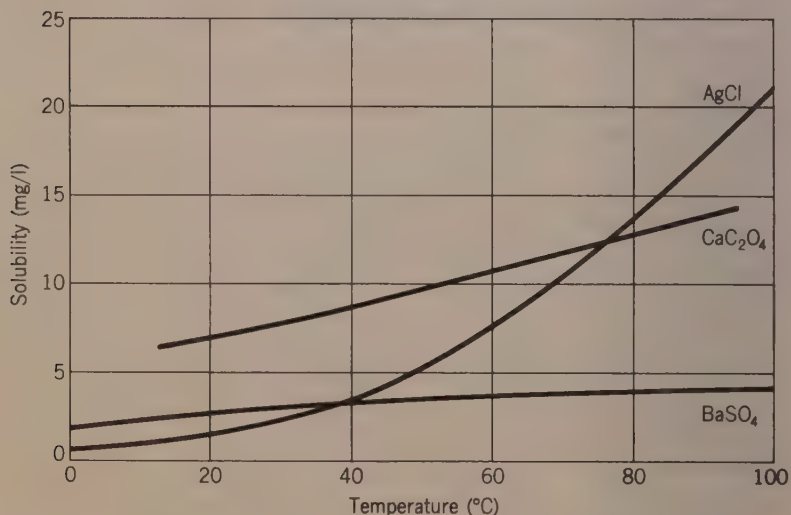


FIG. 11.1. Dependence of Solubility upon Temperature

and the solubilities of such substances do not change much with temperature. A very few substances, such as CaSO_4 and Na_2SO_4 , show a decrease in solubility with an increase in temperature.

Figure 11.1 shows the temperature dependence of the solubilities of a few common gravimetric precipitates (§10). Study of this figure shows that AgCl is about ten times as soluble in hot water (100°C) as it is at room temperature (25°C), whereas BaSO_4 is only about one-half again as soluble. This explains why the AgCl precipitate may not be washed with hot water, whereas BaSO_4 may. The decrease in solubility with decrease in temperature can be used to reduce losses in washing precipi-

tates that are only moderately insoluble. Thus MgNH_4PO_4 is washed with chilled solutions.

Common or reactive ions. The use of a common or reactive ion is the most important single way of producing great changes in solubility. Changes of several hundredfold or several thousandfold, or even more, may be produced.

Suppose that an insoluble salt like Ag_2CrO_4 is dissolved in water to give a saturated solution.



If to this solution there is added a strong electrolyte that has an ion in common with the Ag_2CrO_4 (such as AgNO_3 or K_2CrO_4), the equilibrium is forced back to the left, according to Le Châtelier's principle, and the solubility of Ag_2CrO_4 is much decreased. This effect is employed to reduce solubility losses of precipitates with an excess of precipitant in the mother liquor, or with a common ion in the wash solution. Thus in the gravimetric determination of Ca by precipitation as CaC_2O_4 , the precipitate is washed with a dilute solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4$. No error is caused by retention of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, since it is volatilized when the precipitate is dried and ignited. On the other hand, if a substance that reacts with Ag^+ (such as NH_3) or with $\text{CrO}_4^{=}$ (such as a strong acid) is put into the solution, the solubility of Ag_2CrO_4 is much increased.

Le Châtelier's principle allows prediction as to whether the solubility increases or decreases in the presence of a common or reactive ion, but the magnitude of the effect may be predicted only with the solubility-product principle. The common-ion effect is quantitatively treated in Sec. 11B.5 (p. 167).

Inert electrolytes. See Sec. 11D (p. 171).

Time. Time can have no effect upon a true equilibrium. However, some substances dissolve exceedingly slowly, even with stirring and heating, and some others have a great tendency to remain in the supersaturated condition. If sufficient time is not allowed, the amount of solute per unit volume of solution may not represent the equilibrium solubility at all. The time factor may be an advantage in some analyses, and a disadvantage in others.

The analyst must allow time for precipitation to reach completion. In the formation of some precipitates, such as MgNH_4PO_4 and the phosphomolybdates, the systems must be allowed to stand for several hours to ensure complete precipitation. On the other hand, both MgC_2O_4 and CaC_2O_4 are rather insoluble, yet Ca may be separated from Mg by taking advantage of the fact that MgC_2O_4 has a great tendency to remain in the supersaturated state. CaC_2O_4 precipitates

relatively quickly, and by working fast the analyst may separate it from the mother liquor before MgC_2O_4 comes down.

The low rate of solution of some substances is a great handicap at times. Certain forms of metallic oxides, such as ignited alumina, have a negligible rate of solution even in hot concentrated acids, and must be rendered soluble by fusion with fluxes at high temperatures.

11B. SOLUBILITY PRODUCT

11B.1. The Solubility-Product Principle

The solution of an insoluble, strong electrolyte, like silver chloride, may be represented by



In the saturated solution the following relationship holds, where the bracketed quantities represent molar concentrations* of the solute species whose symbol appears within the brackets, and where K_s is the solubility product.

$$[\text{Ag}^+][\text{Cl}^-] = K_s \quad (11.2b)$$

For a solute like Ag_2CrO_4 ,



For the general solute B_mA_n ,



The molar concentration of any species represents the total concentration of that species in solution, and it may be contributed to by solutes other than the insoluble one. Thus if a solution of K_2CrO_4 is saturated with Ag_2CrO_4 , $[\text{CrO}_4^{=2}]$ is contributed to by two sources, and represents the sum of the $\text{CrO}_4^{=2}$ concentrations obtained from K_2CrO_4 and Ag_2CrO_4 . Also, if Ag_2CrO_4 is dissolved in a solution of HNO_3 , so that some of the $\text{CrO}_4^{=2}$ is bound as the weak acid HCrO_4^- , the bound part does not contribute to $[\text{CrO}_4^{=2}]$.

The *solubility product* is an equilibrium constant for a particular type of reaction—the dissolution of a slightly soluble but highly ionized electrolyte. It must be emphasized that the principle does not describe the behavior of soluble strong electrolytes, or of compounds that exist appreciably in the un-ionized state in solution, such as HgCl_2 (p. 161).

*Of course the solubility-product principle also holds if the ion concentrations are expressed in units other than molarity. However, the literature values of K_s , such as those given in Appendix V, are for molar concentrations. The units of K_s are some power of moles per liter. In Eq. 11.3, K_s has the units (moles/liter)³.

Analytical chemistry is concerned only with the definition and use of the solubility-product principle, not with its derivation. Its proper derivation rests upon thermodynamic principles, and is beyond the scope of this book.

11B.2. Qualitative Interpretation

The solubility-product principle is a quantitative application of Le Châtelier's principle to the equilibrium between the solid solute and the saturated solution. Thus in a saturated solution of Ag_2CrO_4 the function of ion concentrations in Eq. 11.3, $[\text{Ag}^+]^2[\text{CrO}_4^{=}]$, must be constant and equal to K_s . Any alteration of these ion concentrations in the saturated solution results in a spontaneous readjustment of the equilibrium by dissolution or precipitation of solid Ag_2CrO_4 , so that the ion-concentration product readjusts to K_s . For example, (1) if $[\text{CrO}_4^{=}]$ is increased (as by adding K_2CrO_4 to the system), then $[\text{Ag}^+]$ must decrease to maintain the ion product equal to K_s , which means that more solid Ag_2CrO_4 forms, or that the solubility of Ag_2CrO_4 decreases. (2) If $[\text{Ag}^+]$ is diminished, as by adding NH_3 to the system to bind Ag^+ into the soluble complex $\text{Ag}(\text{NH}_3)_2^+$, then $[\text{CrO}_4^{=}]$ must increase to maintain the ion product equal to K_s , which means that more solid Ag_2CrO_4 dissolves, or that its solubility increases.

11B.3. Solubility-Product Tables

Appendix V gives solubility products for some common inorganic substances at room temperature (25°C). In addition to the solubility product K_s , the *solubility-product exponent* pK_s is also given. A small number, such as a K_s value, is sometimes conveniently expressed exponentially. Thus for the quantity X , its pX is the negative log of X .

$$pX = -\log X = \log \frac{1}{X} \quad (11.5)$$

$$pK_s = -\log K_s = \log \frac{1}{K_s} \quad (11.6)$$

An ionization constant is often expressed in terms of its exponent. Hydrogen-ion concentration is very commonly expressed as $p\text{H}$.

Example 1.* What is pK_s if $K_s = 2.0 \times 10^{-16}$?

$$pK_s = -\log (2.0 \times 10^{-16}) = -\log 2.0 - \log 10^{-16} = -0.30 + 16 = 15.70$$

*A review of logarithms is given in Appendix I (p. 901).

Example 2.* What is K_s if $pK_s = 12.35$?

$$\log \frac{1}{K_s} = 12.35$$

$$\frac{1}{K_s} = 10^{12.35} = 10^{12} \times 10^{0.35} = 2.24 \times 10^{12}$$

$$K_s = \frac{1}{2.24 \times 10^{12}} = 4.46 \times 10^{-13}$$

11B.4. Solubility Product Related to Solubility

The solubility product of a solute may be computed from its solubility, and vice versa, as shown in the following examples. Also calculable is the concentration of any solute ion in the saturated solution.

Example 1. The solubility of Ag_2CrO_4 is 2.3 mg/100 ml at 25°C. Compute the solubility product.



$$\left(\begin{array}{c} \text{Solubility} \\ \text{of } \text{Ag}_2\text{CrO}_4 \end{array} \right) = \frac{0.0023}{331.73} \times \frac{1000}{100} = 6.9 \times 10^{-5} M$$

$\underbrace{\hspace{10em}}_{\text{moles/l}} \quad \underbrace{\hspace{10em}}_{\text{moles/100 ml}}$

Hence

$$[\text{Ag}^+] = 2 \times 6.9 \times 10^{-5} = 1.38 \times 10^{-4} M$$

$$[\text{CrO}_4^{2-}] = 6.9 \times 10^{-5} M$$

Therefore

$$K_s = (1.38 \times 10^{-4})^2(6.9 \times 10^{-5}) = 1.31 \times 10^{-12}$$

This example indicates how solubility product may be found from a simple measurement of solubility.

Example 2. A solution containing 0.00100 M NaCl and 0.00200 M BaCl_2 is saturated with the insoluble salt BaCl_2 . The Ba^{2+} concentration is measured by analysis of the solution as 0.00038 M . Calculate the solubility product of BaCl_2 .



$$[\text{Ba}^{2+}][\text{Cl}^-]^2 = K_s$$

$$(0.00038)(0.00100 + 2 \times 0.00200 + 3 \times 0.00038)^2 = K_s$$

$\begin{array}{ccccc} \uparrow & & \uparrow & & \uparrow \\ \text{Cl}^- \text{ from NaCl} & & \text{Cl}^- \text{ from BaCl}_2 & & \text{Cl}^- \text{ from BaCl}_2 \end{array}$

$$K_s = 8.8 \times 10^{-11}$$

*A review of logarithms is given in Appendix I (p. 901).

Example 3. The solubility product of Ag_2CrO_4 is 1.29×10^{-12} at 25°C . (a) Calculate the molar solubility of Ag_2CrO_4 in pure water. (b) How many milligrams of Ag^+ are there in 250 ml of the saturated solution?



(a) Letting the molar solubility of Ag_2CrO_4 be x , we have

$$[\text{Ag}^+] = 2x, \quad [\text{CrO}_4^{2-}] = x$$

Therefore

$$(2x)^2(x) = 1.29 \times 10^{-12}$$

$$x = 6.9 \times 10^{-5} \text{ M } \text{Ag}_2\text{CrO}_4$$

(b) If 6.9×10^{-5} mole of Ag_2CrO_4 goes into a liter of solution, there is $2 \times 6.9 \times 10^{-5}$ or 0.000138 mole of Ag^+ per liter, since 1 mole of Ag_2CrO_4 yields 2 moles of Ag^+ , according to the chemical equation.

The milligrams of Ag per 250 ml are

$$0.000138 \left[\begin{array}{l} \times \frac{250}{1000} \\ \text{moles Ag/l} \end{array} \right] \left[\begin{array}{l} \times 107870 \\ \text{mg Ag/250 ml} \end{array} \right] = 3.72 \text{ mg/250 ml}$$

11B.5. The Common-Ion Effect

The solubility product is a more fundamental property of the solute than is the solubility. The great utility of the solubility product is that it permits a quantitative estimation of the effect of a common or reactive ion. The solubility of a substance is an extremely variable quantity, even for a particular temperature and solvent, and depends upon the concentrations of other common or reactive ions in the solution. However, K_s is approximately independent of the concentrations of these common or reactive ions, and may be used to calculate just how the solubility varies with the common- or reactive-ion concentration, as shown in the following examples. The methods of Sec. 3B (p. 16) are helpful in solving the algebraic equations encountered.

Example 1. How many milligrams of Ag^+ are there per 250 ml of 0.100 M K_2CrO_4 saturated with Ag_2CrO_4 at 25°C ?



Letting y be the molar concentration of Ag^+ , we have

$$[\text{Ag}^+] = y, \quad \text{and} \quad [\text{CrO}_4^{2-}] = 0.100 + \frac{y}{2}$$

From K_2CrO_4 .
From Ag_2CrO_4 .

Therefore

$$(y)^2 \left(0.100 + \frac{y}{2} \right) = 1.29 \times 10^{-12}$$

To solve, assume that the solubility of Ag_2CrO_4 is small, so that the CrO_4^{2-} from the Ag_2CrO_4 is negligible compared to the CrO_4^{2-} from the K_2CrO_4 , or that $y/2$ is negligible compared to 0.100. Then

$$(y)^2 \left(0.100 + \frac{y}{2} \right) = 1.29 \times 10^{-12}$$

$$y = 3.59 \times 10^{-6} M$$

The assumption may be checked by noting that $y/2$, or 1.8×10^{-6} , is much less than 0.100.

From the molar Ag^+ concentration, the milligrams of Ag^+ per 250 ml may be calculated.

$$3.59 \times 10^{-6} \left[\begin{array}{c} \times \frac{250}{1000} \\ \text{moles Ag/250 ml} \end{array} \right] \times 107870 = 0.097 \text{ mg Ag/250 ml}$$

moles Ag/l

Example 2. What is the solubility of Ag_2CrO_4 in 0.00030 M K_2CrO_4 at 25°C?



Letting z be the molar solubility of Ag_2CrO_4 in 0.00030 M K_2CrO_4 , we obtain

$$[\text{Ag}^+] = 2z, \quad \text{and} \quad [\text{CrO}_4^{2-}] = z + 0.00030$$

From Ag_2CrO_4 ↑ ↑ From K_2CrO_4

Therefore

$$(2z)^2(z + 0.00030) = 1.29 \times 10^{-12}$$

Assuming that z is much less than 0.00030, we have

$$(2z)^2(z + 0.00030) = 1.29 \times 10^{-12}$$

$$z = 0.33 \times 10^{-4} M$$

This answer is not a good one, and should be regarded only as a first approximation, for z is *not* much less than 0.00030, as was assumed.

As a second approximation, assume that

$$(z + 0.00030) = 0.33 \times 10^{-4} + 0.00030 = 0.000333$$

Then

$$(2z_2)^2(0.000333) = 1.29 \times 10^{-12}$$

$$z_2 = 0.31 \times 10^{-4} M$$

Third and subsequent approximations also give $z = 0.31 \times 10^{-4} M$ for the solubility of Ag_2CrO_4 .

After the manner of Exs. 1 and 2, the solubilities of Ag_2CrO_4 in solutions of K_2CrO_4 at various concentrations may be calculated and plotted as in Fig. 11.2. Inspection of Fig. 11.2 yields the following conclusions: (1) A point of diminishing returns is eventually reached, where adding rather large amounts of K_2CrO_4 does not appreciably decrease the solu-

bility of Ag_2CrO_4 further. (2) Precipitation is never absolutely complete, no matter how large an excess of common ion is used. In quantitative analysis, precipitation is regarded as "complete" if the amount of

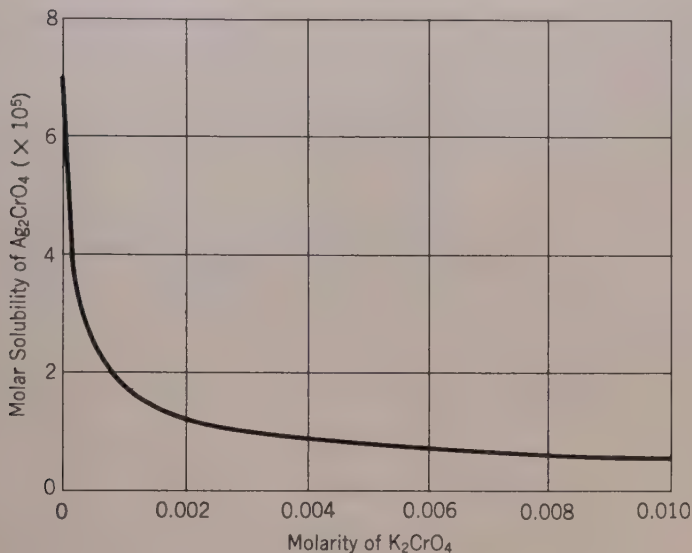


FIG. 11.2. Solubility of Ag_2CrO_4 in the Presence of K_2CrO_4 , Calculated (25°C)

sought-for substance remaining in solution causes an error considerably less than the acceptable error. For example, if the weight of a precipitate is 1 g, and if an error of 0.1% is acceptable, the loss of a few tenths of a milligram in the supernatant and wash liquids is negligible.

Example 3. A 50.0-ml portion of 0.100 M AgNO_3 is mixed with a 25.0-ml portion of 0.156 M K_2CrO_4 . Give the composition of the solution at equilibrium, the amount of Ag_2CrO_4 that precipitates, and the percentage of the Ag left in solution.

After mixing, but before reaction, there are present in $50.0 + 25.0 = 75.0$ ml:

$$\text{Moles AgNO}_3 = 0.100 \times \frac{50.0}{1000} = 0.00500$$

$$\text{Moles K}_2\text{CrO}_4 = 0.156 \times \frac{25.0}{1000} = 0.00390$$

Since there is an excess of K_2CrO_4 , it may be assumed as a first approximation that precipitation of Ag^+ is complete. Since one mole of Ag^+ yields one-half mole of Ag_2CrO_4 ,

$$\text{Moles Ag}_2\text{CrO}_4 \text{ precipitated} = \left(\frac{1}{2}\right)(0.00500) = 0.00250$$

$$\text{Grams Ag}_2\text{CrO}_4 \text{ precipitated} = 0.00250 \times 331.73 = 0.83 \text{ g}$$

The moles of K_2CrO_4 left are $0.00390 - 0.00250$, or 0.00140 , which in a volume of 75.0 ml gives a concentration of

$$0.00140 \times \frac{1000}{75.0} = 0.0187 \text{ } M \text{ } K_2CrO_4$$

The previous approximation is made only to find the composition of the solution after reaction. Actually, some Ag will be left in solution, for the Ag_2CrO_4 is not completely insoluble. Letting $[Ag^+] = x \text{ } M$,

$$[CrO_4^{2-}] = \frac{x}{2} + 0.0187$$

From the solubility product for Ag_2CrO_4

$$[Ag^+]^2[CrO_4^{2-}] = K_s$$

$$(x)^2 \left(\frac{x}{2} + 0.0187 \right) = 1.29 \times 10^{-12}$$

$$x, \text{ or } [Ag^+] = 8.3 \times 10^{-6} \text{ } M$$

Hence at equilibrium

$$\text{Moles } Ag_2CrO_4 \text{ precipitated} = 0.00250 - \frac{1}{2} \left(8.3 \times 10^{-6} \times \frac{75.0}{1000} \right)$$

Negligible, justifying previous assumptions. \nearrow

$$[Ag^+] = 8.3 \times 10^{-6} \text{ } M$$

$$[CrO_4^{2-}] = 0.0187 + \frac{1}{2}(8.3 \times 10^{-6}) \text{ } M$$

Negligible. \nwarrow

$$[K^+] = 2 \times 0.156 \times \frac{25.0}{75.0} = 0.104 \text{ } M$$

$$[NO_3^-] = 0.100 \times \frac{50.0}{75.0} = 0.067 \text{ } M$$

Percentage of total Ag left in solution is

$$8.3 \times 10^{-6} \left| \begin{array}{l} \times \frac{75}{1000} \\ \times \frac{100}{0.00500} \end{array} \right| = 0.0125\%$$

Total moles Ag originally present. \nwarrow

moles Ag/75 ml \nwarrow

moles Ag/l \nwarrow

11C. APPLICATIONS OF SOLUBILITY THEORY IN QUANTITATIVE ANALYSIS

Computation of solubility losses. Losses of a sought-for precipitate in the supernatant and wash liquids may be calculated from solubility-product theory. Such losses may safely be regarded as maximum losses, since the wash liquid may not be in contact with the precipitate long enough to become saturated. In all cases, however, such calculated

losses should be regarded only as rough approximations, because of the neutral electrolyte effect. (See below.)

Reduction of solubility losses. The objective in quantitative analysis is to reduce solubility losses to negligible proportions. Several methods may be used: (1) The most effective way is to use a common ion in the supernatant liquid, and also in the wash liquid, if possible. Other accepted methods of reducing solubility losses are (2) use of a minimum quantity of wash liquid, (3) use of a cold wash liquid, and (4) use of a wash liquid containing a nonaqueous solvent. (5) If there is a tendency toward supersaturation, sufficient time must be allowed for complete precipitation.

Selection of optimum conditions for analysis. To keep error low, the conditions of any analysis must usually be carefully selected to eliminate interferences and to achieve high recovery of the sought-for substance. In designing or altering such a method, calculations involving solubility product (and other equilibrium constants) are often necessary.

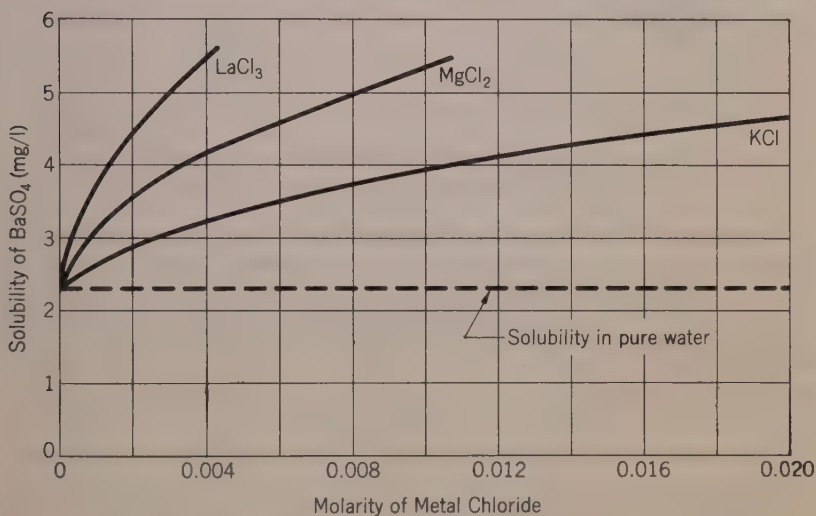


FIG. 11.3. Solubility of BaSO_4 in Solutions of Electrolytes at 25°C

11D. THE INERT-ELECTROLYTE EFFECT

In the elementary treatment, it is assumed that K_s for a substance is quite independent of the concentration of other electrolytes that may be present. This is only approximately true, as shown in Fig. 11.3, which is a plot of experimental solubilities of BaSO_4 in the presence of various electrolytes (S10). The increase in solubility of BaSO_4 with concentration of an inert electrolyte containing no common or reactive ion

is called the *inert-electrolyte effect*, and is greater for electrolytes with highly charged ions. This effect is large, amounting to an increase of several-fold for rather low concentrations of inert electrolyte; and it is unexpected from the definition of solubility product given previously, according to which the solubility of BaSO_4 in such solutions should be constant, and should fall along the dotted horizontal line in Fig. 11.3.

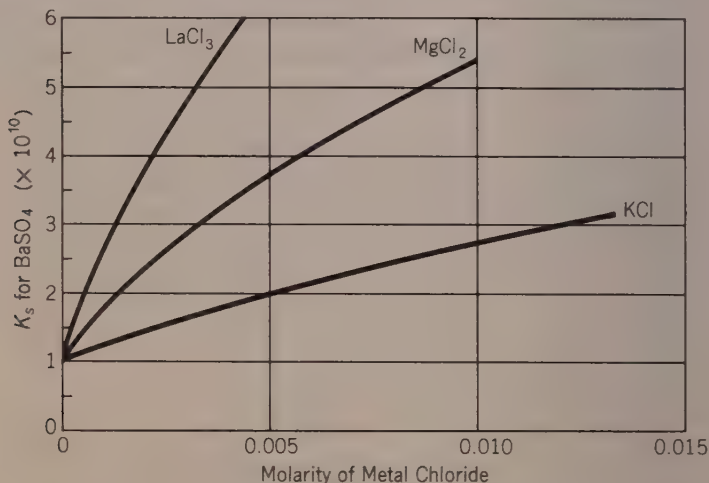


FIG. 11.4. K_s of BaSO_4 in Solutions of Various Electrolytes

K_s values for BaSO_4 may be calculated for each of the solubilities in Fig. 11.3 as in the following example, and plotted as in Fig. 11.4. It may be seen that K_s is not constant, but increases with inert-electrolyte concentration. Solubilities calculated from elementary theory as in the preceding parts of this chapter may be considerably in error owing to the inert electrolyte, even in dilute solutions, and particularly when ions of multiple charge are involved. This increase in K_s and in solubility is due in part to the electrostatic attraction between the inert-electrolyte ions in solution and the ions in the crystal lattice of the solid. The quantitative treatment of the inert-electrolyte effect is given in the Supplement (p. 701). The accuracy of solubility-product calculations is also discussed in the Supplement (p. 704).

Example. Compute K_s for BaSO_4 from its solubility in 0.0110 M KCl , given in Fig. 11.3.

$$\text{Solubility of } \text{BaSO}_4 = \frac{0.0040}{233.40} = 1.71 \times 10^{-5} M$$

moles/l

$$K_s = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (1.71 \times 10^{-5})(1.71 \times 10^{-5}) = 2.9 \times 10^{-10}$$

Note that this is about threefold greater than the value of K_s in pure water.

QUESTIONS

Section 11A

1. Is heat evolved or absorbed during dissolution, if the solubility of a substance decreases as temperature increases?

2. From Fig. 11.1 (p. 162), determine whether the heat absorbed upon dissolving a mole of AgCl is greater or less than the heat absorbed upon dissolving a mole of BaSO_4 .

3. Solubility losses are often appreciable in an ordinary analysis, even when "insoluble" precipitates like AgCl , BaSO_4 , and CaC_2O_4 are formed. Support this statement by the data in Fig. 11.1.

4. Write ionic equations showing the effects of NH_3 or H_3O^+ on the solubility of Ag_2CrO_4 .

5. List several substances that would affect the solubility of CaC_2O_4 by virtue of the common- or reactive-ion effect, and explain the action of each, using ionic equations.

6. Discuss the effect of pH on the solubility of MgNH_4PO_4 .

Section 11B

1. For $\text{Pb}(\text{IO}_3)_2$, give the units of K_s in Appendix V.

2. How would K_s for SrSO_4 in water compare with that in a 50-50 alcohol-water mixture?

3. In Table 4.1 (p. 22) indicate the class of substances for which the solubility-product principle holds. Indicate the classes for which it does not hold, explaining why in each case.

4. What is meant by saying that the solubility-product principle expresses a relationship? Define the principle in words, and discuss the relationship.

5. Why is it more useful to state that the solubility product of AgCl is 1.0×10^{-10} than to say that the solubility in pure water is $1.0 \times 10^{-6} M$?

6. If the solubility of a substance, AB , is $1.0 \times 10^{-5} M$ in pure water, is it always correct to infer that the solubility product is 1.0×10^{-10} ? What other information must be known before this inference may be made?

7. Explain why precipitation is never complete, using the solubility-product concept.

8. Can the solubility product for a binary salt ever equal the cube of its molar solubility? For what type of salt would such a relation hold?

9. Explain whether $0.01 M \text{AgNO}_3$ or $0.01 M \text{K}_2\text{CrO}_4$ would be more effective in repressing the solubility of Ag_2CrO_4 .

10. Four salts and their solubility products are: WA , K_1 ; XB , K_2 ; YA_2 , K_3 ; ZB_2 , K_4 . Is it correct to say that the molar solubility of (a) WA is greater than that of XB , if $K_1 > K_2$? (b) YA_2 is greater than that of ZB_2 , if $K_3 > K_4$? (c) WA is greater than that of ZB_2 , if $K_1 > K_4$? (d) ZB_2 is greater than that of WA , if $K_4 > K_1$?

Section 11C

1. Why does one usually worry less about loss of a precipitate in the mother liquor than in pure water wash solutions?

2. Would it be practicable to use the common-ion effect in reducing losses in washing AgCl (a) in gravimetric analysis of KCl-NaCl mixtures? (b) in gravimetric analysis of $\text{AgNO}_3\text{-KNO}_3$ mixtures?

3. Occasionally, a wash solution that is saturated with respect to the sought-for

precipitate is recommended in order to reduce solubility losses if the precipitate is only moderately insoluble (K_{18}). What precautions should be taken if this method is used?

PROBLEMS

Section 11A

1. From the solubility of BaSO_4 in Fig. 11.1 (p. 162), how much hot (90°C) wash water may be used for washing if a loss of 1.0 mg is tolerable? Would it be practicable to try to reduce solubility losses to 0.1 mg simply by restricting the volume of wash water in a gravimetric determination? *Ans.* 240 ml; no.

2. From Fig. 11.1, compute the solubility loss in washing an AgCl precipitate with 250 ml of water at (a) 20°C , (b) 95°C . Repeat the calculations for BaSO_4 . Compute the percentage losses, if the weight of each precipitate is about 0.50 g.

Section 11B

1. In order to determine the solubility product of AgCl , dilute NaCl solution is titrated into AgNO_3 until the first appearance of a precipitate. Just before this point is reached, the concentrations of AgNO_3 and NaCl are 3.3×10^{-5} and $0.8 \times 10^{-5} M$, respectively. What is K_s for AgCl , and why may this value be high? *Ans.* 2.6×10^{-10} .

2. The solubility of BaSO_4 in water is 3.0 mg/l at 40°C . Compute the solubility product.

3. Compute the solubility product if the solubility of Ag_2CO_3 is 34 mg/l at 15°C . *Ans.* 7.5×10^{-13} .

4. Calculate the solubilities of the following salts in water, giving answers in milligrams per 250 ml: (a) CaSO_4 , (b) AgI , (c) $\text{Pb}(\text{IO}_3)_2$, (d) Hg_2Cl_2 .

5. How many times is the solubility of AgCl increased on raising the temperature from 0 to 100°C ? How many times is K_s increased? *Ans.* 22-fold; 480-fold.

6. Express the relationship between the molar solubility s and K_s for the following types of salts: (a) AgCl , (b) BaSO_4 , (c) $\text{Ba}(\text{IO}_3)_2$, (d) A_2B_3 ($\text{A}_2\text{B}_3 \rightleftharpoons 2\text{A}^{3+} + 3\text{B}^{-}$).

7. Each of two unlabeled test solutions contains 10 mg/ml of $\text{Pb}(\text{NO}_3)_2$ and of AgNO_3 , respectively. Based on the use of 0.1 M HCl as the only reagent, outline a simple procedure to identify the two solutions.

Ans. $\text{Pb}(\text{NO}_3)_2$ solution will not give a precipitate if mixed 1:1 with 0.1 M HCl , whereas AgNO_3 solution will.

8. From some of the K_s values in Appendix V, calculate the corresponding pK_s values. From some of the pK_s values, calculate the corresponding K_s values.

9. (a) If $K_s = 10^{-6.00}$, what is pK_s ? (b) If $K_s = 3.0 \times 10^{-7}$, what is pK_s ? (c) If $pK_s = 11.85$, what is K_s ? *Ans.* (b) 6.52.

10. Give the composition of 0.025 M Na_2SO_4 saturated with PbSO_4 .

11. Give the composition of 0.010 M $\text{Mg}(\text{IO}_3)_2$ saturated with $\text{Pb}(\text{IO}_3)_2$.

Ans. $[\text{Mg}^{2+}] = 0.010 M$, $[\text{Pb}^{2+}] = 7.2 \times 10^{-10} M$, $[\text{IO}_3^-] = 0.020 M$.

12. What is the relation between the molar solubilities of the substances AB and A_2C , if the solubility products are numerically equal?

13. Find the fraction of the original sulfate left in solution after addition of 1.0 g/l of $\text{Ba}(\text{NO}_3)_2$ to each of the following solutions saturated with BaSO_4 : (a) pure water; (b) 0.010 M $\text{Ba}(\text{NO}_3)_2$. *Ans.* (a) 0.0026; (b) 0.7.

14. Solid NaOH is added to a solution that originally contains 0.0100 M FeCl_3 and 0.0100 M MgCl_2 , without any significant change in volume. Calculate: (a) the

pH when $\text{Fe}(\text{OH})_3$ starts to precipitate, (b) the pH when $\text{Mg}(\text{OH})_2$ starts to precipitate, (c) the concentration of Fe^{3+} remaining in solution just before $\text{Mg}(\text{OH})_2$ starts to precipitate.

Section 11C

1. The following exercise is on the efficiency of washing:

(a) Let X be the amount of soluble impurities contained in the mother liquor of volume L , originally associated with the sought-for precipitate. The mother liquor is filtered off, but the precipitate mechanically retains a volume v of the contaminated mother liquor. What are the amount and fraction of the original impurities remaining on the precipitate?

Ans. $X(v/L), v/L$.

(b) A volume V of wash liquid is now added to the precipitate on the filter, so that the impurities become diluted to a volume $v + V$, which is then drained off so that only the volume v is retained on the precipitate. What fraction of the original impurity remains after this first washing?

$$\text{Ans. } \left(\frac{v}{L}\right) \left(\frac{v}{V+v}\right).$$

(c) What fraction of the original impurities remains after the n th wash portion of volume V ?

$$\text{Ans. } \left(\frac{v}{L}\right) \left(\frac{v}{V+v}\right)^n.$$

(d) Approximate the answers to part c if $v \ll V$.

Ans. $(v/L)(v/V)^n$.

(e) It is decided in a particular analysis that the total volume of wash liquid must be restricted to 200 ml. Using the results of part d, estimate the fraction of original impurities remaining on the precipitate after each of the following washing processes: (1) one wash of 200 ml; (2) two washes of 100 ml; (3) three washes of 67 ml; (4) four washes of 50 ml; (5) five washes of 40 ml. Assume that $v = 2$, $L = 200$ ml. Describe the best way to utilize a given portion of wash liquid for maximum washing efficiency.

2. Assume that 100 ml of wash liquid are to be used. What is the minimum number of portions that could be used to reduce the impurities originally associated with the precipitate in the mother liquor by a factor of 10^6 ? Assume that $v = 2$, $L = 100$.

3. Compute the milligrams of AgCl left unprecipitated in 350 ml of a mother liquor containing 0.0010 M AgNO_3 . Compare this figure with the amount dissolved in 350 ml of pure wash water containing no common ion, and state the relative importance of losses in the mother and wash liquids.

Ans. .0090 mg, 0.67 mg.

4. Assuming no supersaturation, what volume of water is required to dissolve 0.20 mg Ag_2CrO_4 ?

5. How many milligrams of $\text{Pb}(\text{IO}_3)_2$ dissolve in 300 ml of (a) pure wash water, (b) a solution containing 0.010 M $\text{Pb}(\text{NO}_3)_2$?

Ans. (a) 6.9 mg; (b) 0.45 mg.

6. A BaSO_4 precipitate is washed with 1.00 l of a solution containing 1.00 g H_2SO_4 per liter. What is the loss (in mg) of BaSO_4 in this wash solution?

7. After 3.0 mmoles of AgNO_3 are dissolved in water, 2.0 mmoles of K_2CrO_4 are added, at which point the volume is 227 ml. How much Ag remains unprecipitated, and what percentage of the total Ag is this?

Ans. 0.6 mg, 0.18%.

8. A 0.1699-g portion of AgNO_3 is dissolved in pure water to give 200 ml of solution. What weight of K_2CrO_4 must be added to reduce the weight of AgNO_3 in solution to 1.0 mg?

9. If strontium is determined gravimetrically by precipitating SrSO_4 , what must

be the sulfate-ion concentration in the wash liquid in order that the loss of Sr^{2+} will not exceed 0.10 mg/100 of solution? *Ans.* 0.028 *M*.

10. How much Ag remains unprecipitated after 65.0 ml of 0.120 *M* KCl are added to 50.0 ml of 0.10 *M* AgNO_3 ? What percentage of the total Ag is this?

11. The theoretical amount of 0.0100 *M* BaCl_2 (plus an excess of 10%) is added to 100.0 ml of a solution containing 3.0 mmoles of K_2SO_4 . What percentage of the sulfate remains in solution? *Ans.* 0.0021%.

12. A 0.927-g sample contains 62% K_2CrO_4 , and is dissolved to give 100 ml of solution. (a) Calculate the volume of 0.100 *M* AgNO_3 required for precipitation, plus a 10% excess. (b) If this volume of AgNO_3 is added, find the percentage of chromate unprecipitated. (c) If the precipitate is washed with 100 ml of water, what is the percentage loss of chromate due to washing?

12 THE FORMATION OF PURE PRECIPITATES

12A. PROPERTIES OF PRECIPITATES DESIRABLE FOR GRAVIMETRIC ANALYSIS

It is desirable that a precipitate to be weighed in a gravimetric analysis should have the following properties: (1) The solubility should be low so that losses are negligible. Unfortunately, many of the so-called "insoluble" substances have appreciable solubilities, and sometimes considerable effort is necessary to avoid serious solubility losses. (2) The precipitate should be easily filterable and washable. The particles must not be so fine that they pass through the filter, nor must they be so large that they entrap impurities and mother liquor that cannot be washed out. (3) The precipitate should be stable and of definite composition, or easily convertible to such a substance; otherwise the amount of sought-for substance may not be accurately estimated from the measured weight of precipitate. In this connection, the precipitate should be easy to dry and stable in air, so that it may be conveniently weighed. It must be pure, and should have no tendency to carry along other substances that may be present during formation. (4) The precipitant should be as selective as possible for the sought-for substance, so as to avoid troublesome separation of interferences. (5) A small amount of sought-for substance should yield a relatively large amount of precipitate. Then the method is sensitive.

The perfect realization of all these factors is never possible; in fact, some are mutually exclusive. In any analysis a compromise is necessary, and conditions are chosen so that the foregoing requirements are

optimally satisfied. Very often, departure from the optimum conditions to achieve a fuller realization of one of these properties results in a loss in one or more of the others.

Properties 4 and 5, although desirable, are not on the same level of importance as the first three. This chapter considers the factors upon which properties 2 and 3 depend, and the means used to control these factors.

12B. FORMATION OF PRECIPITATES

Solubility-product theory permits statements about the solubility of a precipitate under certain conditions, and about the factors upon which the solubility depends. But it gives no information about other characteristics of the precipitate, which depend upon the mode of formation.

Precipitate formation is a kinetic or dynamic process—that is, one which is proceeding toward equilibrium, and in which the composition and properties of the system are time dependent. Control of the rate and of other conditions under which precipitation occurs permits control of the properties of the resulting precipitate. In this section, the mechanism of crystallization and the variables that affect it are studied, so that it may be controlled.

12B.1. Outline of the Precipitation Process

To form a precipitate it is necessary to start with a supersaturated solution of the substance. The supersaturated state is unstable, and changes to the saturated state by precipitation of the excess solute. The rate at which equilibrium is attained depends upon many factors and may vary tremendously from one substance to another; it may vary even for the same solute under different conditions. The precipitation process is depicted schematically in Fig. 12.1.

The first step in precipitation is *nucleation*. The mode of formation and the size of the primary particles are not yet known, though there is evidence that the particles are only a few ion pairs in size. The rate of formation of nuclei increases very rapidly with the degree of supersaturation. The nuclei are not stable, and they change by growing to larger, *colloidal particles*, which are not filterable by ordinary means.

Once colloidal particles are formed, the process may take either of two paths, depending on whether or not supersaturation still exists. If the solution is no longer supersaturated, the colloidal particles may remain as such; or if given time enough, or if forced, they may agglomerate to larger filterable *colloidal aggregates*. Methods of forcing the

point representing the solution moves left on the diagram. No crystallization occurs, even when the point *b*, representing saturation, is attained. If the system is clean, with no solid particles to act as seeds, the solution may be cooled further, bringing it into the supersaturated

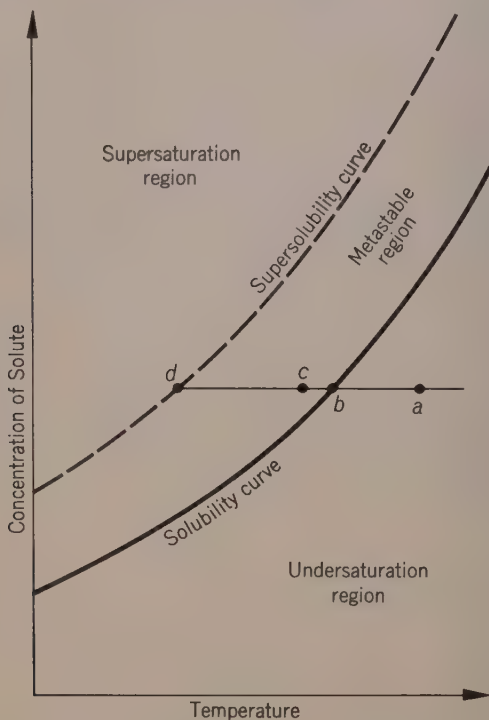


FIG. 12.2. Supersaturation and the Solubility Curve

region. If the cooling is stopped at some point, *c*, close to the solubility curve, the system is metastable—that is, it may survive indefinitely in the supersaturated state. In order to form nuclei at a good rate, it is generally necessary to cool the system appreciably beyond the saturation curve, to a degree of supersaturation represented by the supersolubility curve, that is, to point *d* on the diagram.

The dependence of rate of nucleation upon the degree of supersaturation is shown in Fig. 12.3. For low degrees of supersaturation, the rate of nucleation may be so low that nucleus formation is virtually nil, and the system is regarded as metastable. On the other hand, when the degree of supersaturation exceeds values represented by the supersolubility curve, the nucleation rate increases almost explosively with the degree of supersaturation.

12B.3. Crystal Growth

Once formed, a nucleus may grow larger by the regular process of crystallization, in which individual molecules are attracted from solution and incorporated one at a time into the crystal lattice structure:



The rate of such a monomolecular process is proportional to concentration, and the rate of growth of nuclei (once formed) depends linearly upon the degree of supersaturation, as shown in Fig. 12.3. Further details are given in the Supplement (p. 717).

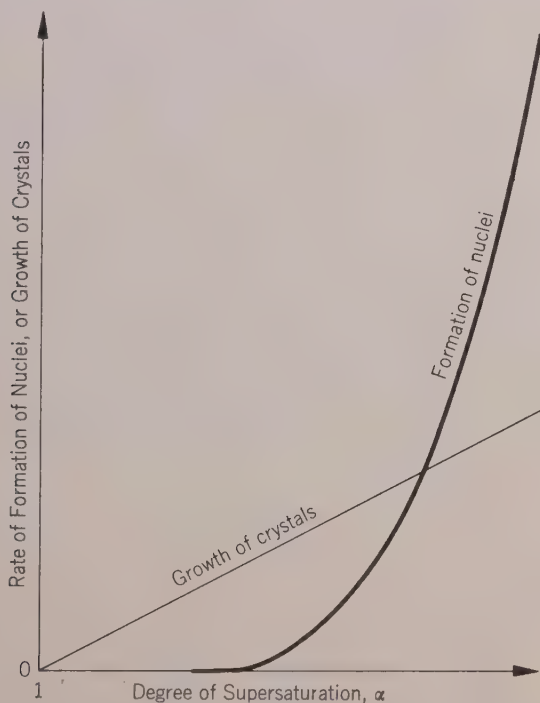


FIG. 12.3. Formation of Nuclei and Growth of Crystals

12B.4. Precipitate Formation

When a precipitate is formed, both nucleation and growth go on simultaneously, the relative importance of the two changing throughout the precipitation process. Thus, at the very beginning, nucleation must be the predominant process, but at the very end, growth must be predominant. The very beginning and very end, however, are only insign-

nificant fractions of the whole process, and the bulk of precipitate is formed during an interval when predominance transits from nucleation to growth.

Further, a real precipitation process never occurs in a single stage during which the degree of supersaturation starts at a high value and diminishes uniformly to zero. Not only does the degree of supersaturation vary locally throughout the precipitation vessel, but precipitation occurs even while precipitant is being added. In short, the degree of supersaturation is nonhomogeneous and poorly defined with respect to both space and time.

It is not surprising, therefore, that quantitative experimental verification of the theories of nucleation and growth is exceedingly difficult, and that the above pictures of the processes are highly idealized. Despite their simplicity and shortcomings, however, the above nucleation and growth mechanisms permit useful generalizations about the practices required to produce certain characteristics in precipitates.

With the aid of Fig. 12.3, two extreme sets of conditions may be visualized for the precipitation process. At a low degree of supersaturation, nuclei form at a very low rate, and cannot relieve supersaturation significantly. After the first few nuclei are formed, their rate of growth is much larger than the rate of formation of more nuclei. Hence, practically all of the supersaturation goes into the growth of a few nuclei, which can therefore become large, as in a coarsely crystalline precipitate.

At high supersaturation, a burst of nucleation occurs, giving many nuclei. The remaining supersaturation is relieved by further growth of the nuclei, but since there are so many, none can grow large. A finely crystalline or colloidal precipitate results.

The classical experiments of von Weimarn (v5) are summarized in Table 12.1, and illustrate how the degree of supersaturation determines the character of the precipitate.

Coarsely crystalline precipitates are most desirable for gravimetric analysis. Such precipitates are formed by path I, Fig. 12.1, and all the particles are well-formed, individual crystals. These precipitates are rather dense, settle rapidly, and often show a silky sheen when observed in the supernatant liquid. Coarsely crystalline precipitates are easy to filter and wash, and do not adsorb or occlude impurities to any great extent. Examples may be found among the more soluble precipitates, such as PbCl_2 , $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$, KClO_4 , and K_2PtCl_6 , or among insoluble ones formed at low degrees of supersaturation.

There are several practices that are commonly used to obtain coarsely crystalline precipitates:

1. High degrees of supersaturation are avoided by adding the precipitate slowly, and in dilute solution.

2. By carrying out the precipitation at elevated temperature, the solubility is increased, and the degree of supersaturation for a particular concentration is diminished.

3. Chemical methods may also be employed to keep the degree of supersaturation low. One way is to throw down the greater portion of the precipitate from a solution in which the precipitate is quite soluble. For example, in precipitating Ca as CaC_2O_4 , the Ca and excess oxalate are mixed together in a solution of sufficiently high acidity to bind $\text{C}_2\text{O}_4^{2-}$ as the weak acid HC_2O_4^- , so that the solubility product of CaC_2O_4

TABLE 12.1

EFFECT OF SUPERSATURATION ON THE NATURE OF THE BaSO_4 PRECIPITATE

MOLARITY OF $\text{Ba}(\text{SCN})_2$ AND MnSO_4 SOLUTIONS*	RELATIVE DEGREE OF SUPER- SATURATION	TIME REQUIRED FOR		NATURE OF PRECIPITATE
		First Appearance of Precipitate	Most of Precipitate to Form	
0.000025-0.00007 0.00010-0.00012	1-3 8-10	None in 1 year 1 week 2 months	None formed. After 6 months, largest crystals are about $15 \times 30 \mu$.
0.0002-0.001	16-80	A few hours to a few sec- onds	1 day to $\frac{1}{2}$ hour	At $5 \times 10^{-4} M$, microcrystals are about $2 \times 3 \mu$ after 3 hours. These grow a little larger after 6 months, the largest crystals being about $4 \times 7 \mu$.
0.001-0.4	80-20,000	Almost in- stantaneous	Microcrystalline skeletons and needles. At 0.1 M, most needles are considerably shorter than 2μ . Crystals are barely recognizable at 0.4 M.
0.4-1.5	20,000-90,000	Instantaneous	Curdy, amorphous precipitates. Particles are barely resolvable at magnification of 1500.
1.5-3.5	90,000-200,000	Instantaneous	Clear jelly is first formed, which does not run out when beaker is inverted. No particles are visible with ultramicro- scope. The gel is unstable, and crystal- lizes rapidly.

* About equivalent quantities of each are poured together. These salts are used because of their high solubilities.

is not exceeded. The acid is then slowly neutralized with NH_3 until the Ca is quantitatively precipitated. This process gives larger crystals than would be obtained by adding oxalate to Ca in a neutral solution.

The technique of homogeneous precipitation provides for very slow and uniform addition of precipitant, so that the degree of supersaturation is very low throughout the whole precipitation process. The homogeneous precipitation process is described in the Supplement (p. 719).

4. Digestion, which is the process of letting the crystals stand for a time in contact with the mother liquor, often causes transformation of small, imperfect, and impure crystals into larger, more perfect, and purer ones.

When it is not possible to obtain coarsely crystalline precipitates, the analyst settles for other types. *Pulverulent* or *finely crystalline precipi-*

tates consist of aggregates of fine crystals, and are formed by path II, Fig. 12.1. They are rather dense and settle rapidly, but are often difficult to filter, since there are always some small crystals present that may pass through the filter. Because of the voids in the aggregates, there is a tendency toward occlusion of impurities. Examples of finely crystalline precipitates are BaSO_4 , BaCrO_4 , and CaCO_3 .

Curdy precipitates, formed by path III, Fig. 12.1, result from aggregation of colloidal particles without much further growth. Examples are AgCl and CuI . Curdy precipitates are often formed from hydrophobic colloids, and are quite dense, since they do not contain much water. There is a tendency to occlude impurities in the voids of the aggregates. Coagulation may be effected by electrolytes, heat, and stirring, but care must sometimes be exercised in washing to prevent peptization and loss.

Colloidal particles do not always coagulate to curdy precipitates. If the colloid is a hydrophilic one, very bulky, flocculent, or *gelatinous precipitates* that contain much water may be obtained. Common precipitates of this type are $\text{Fe}(\text{OH})_3$, $\text{Al}(\text{OH})_3$, hydrated silica, and some sulfides. Because of their bulk they are difficult to wash and filter. The use of suction with such precipitates packs them into an impervious film upon the filter surface and retards, rather than hastens, filtration.

12C. THE COLLOIDAL STATE. ADSORPTION (M25)

12C.1. Description of the Colloidal State

Whenever filterable precipitates are formed, the system must pass through the colloidal state, in which the particles have diameters of $0.001\text{--}0.1\ \mu$. Systems in this state possess unique properties because of the small particle sizes. With the ordinary light microscope such particles are not visible, and the systems seem to be homogeneous, true solutions. Colloidal systems also behave like true solutions in that the particles cannot be separated by filtration through ordinary filters, or by settling in the earth's gravitational field. And yet, because the particles are so much larger than molecules, they exert almost no effect on the properties of the solvent (freezing point, boiling point, vapor pressure, osmotic pressure); in this respect colloidal systems do not act like true solutions at all.

Because of these contradictory properties, colloidal systems were originally thought unique. It is now realized, however, that their properties lie between those of true solutions and suspensions. Colloidal particles are visible with an ultramicroscope, and they may be isolated with an ultrafilter (very fine pores) or an ultracentrifuge (very high speeds). Furthermore, colloidal systems may be considered to be solutions of

solutes of very high molecular weight, because the colloidal particles are much larger than ordinary molecules, and precise study shows that they exert the same slight effect on solvent properties (freezing point, etc.) that would be expected of any solute of very high molecular weight.

In gravimetric analysis the colloidal state is studied primarily to learn how it may be avoided in preparing precipitates, and also to learn how to reduce the carrying of impurities acquired in passing through this state. It must not be supposed, however, that the principles learned in such a study are so restricted. In many applications the concern is not to avoid the colloidal state but to maintain it. And, furthermore, the principles studied are just those underlying the wide use of ion exchange and adsorption in separations and in recovery of traces of substances.

Before proceeding, it is necessary to define some terms that are used repeatedly in the following sections. A system is *homogeneous* if the smallest isolable part has the same properties as any other part. A true solution is homogeneous. A system is *heterogeneous* if different small isolable parts have different properties. A suspension of CaCO_3 in its saturated solution is heterogeneous. A *phase* of a system consists of all parts having identical properties: a homogeneous system contains only one phase, but heterogeneous systems contain more than one phase. In the foregoing suspension of CaCO_3 , the solid CaCO_3 is one phase, and the saturated solution is the other. This chapter is devoted almost exclusively to two-phase systems of solids in liquids, but there are all sorts of other systems containing solid, liquid, and gaseous phases. A phase may be *dispersed*, as when different parts of the same phase are separated from each other in the system, or a phase may be *continuous*, as when the parts of the phase are connected throughout the system. In some cases, as in a gel, such a distinction cannot be made, for the phases are interwoven. In the example above, CaCO_3 is the dispersed phase, and the solution is the continuous one. The *components* of a system are the minimum number of individual chemical substances that make up the system: CaCO_3 and H_2O are the components of the CaCO_3 suspension in water. *Peptization* and *dispersion* are the names given to the process of breaking down large, filterable particles into smaller, colloidal ones. When colloidal particles come together and stick to form larger, filterable masses, the process is called *agglomeration*, *coagulation*, or *aggregation*.

12C.2. The Adsorption Process

Figure 12.4 represents a colloidal AgCl particle bathed in a solution containing NaCl , a strong electrolyte. The electrostatic fields of force of the surface ions extend into the solution, attracting oppositely charged

solute ions (Na^+ , Cl^-) into the *adsorbed-ion layer*. If only electrostatic forces were operative, there would be no preponderance of positive over negative charges in the adsorbed-ion layer. However, ions in the adsorbed-ion layer are close enough to the solid surface ions so that strong short-range *van der Waals and chemical bonding forces* become operative. These short-range forces are highly specific, and permit preferential

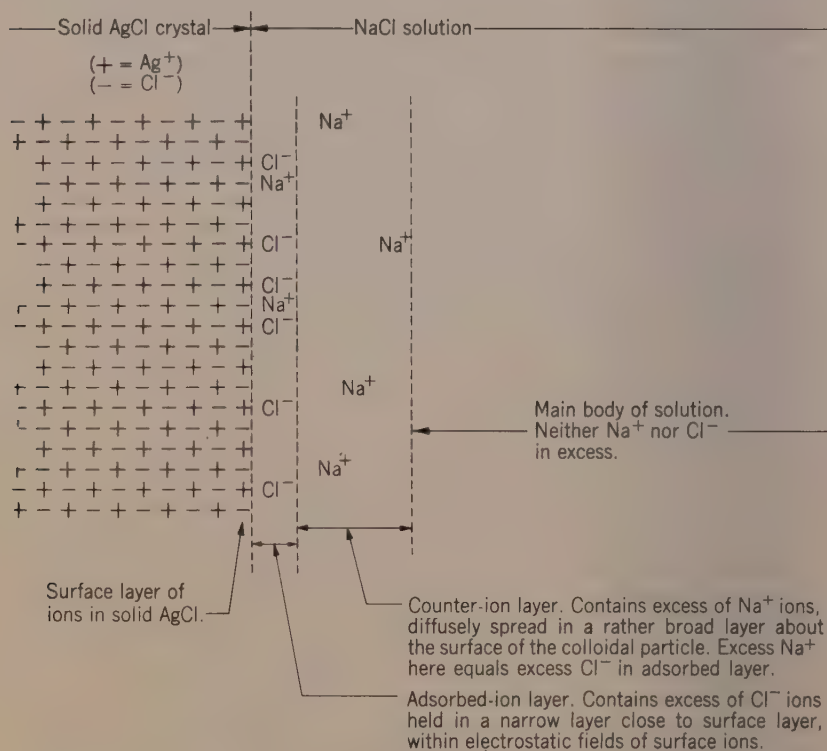
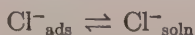


FIG. 12.4. Diagram of the Colloidal Particle and the Adsorption Process

adsorption of one kind of ion over another. In the case at hand, the tendency of surface Ag^+ to attract Cl^- from solution is stronger than the tendency of surface Cl^- to attract Na^+ from solution, and therefore an excess of Cl^- is built up in the adsorbed-ion layer. This is how colloidal particles acquire a charge. A colloidal particle with its adsorbed-ion layer may be regarded as an ion of very high molecular weight and high charge.

There is a limit to the number of ions that can be held in the adsorbed-ion layer. When enough like-charged ions become adsorbed, the repul-

sive electrical forces among them become equal to the attractive adsorption forces, and equilibrium is reached between the adsorbed ions and the ions in solution:



This equilibrium is dynamic; any particular adsorbed Cl^- does not remain permanently associated with a particular lattice Ag^+ ; the adsorbed Cl^- remains for a while and then floats out of the adsorbed-ion layer and back into solution. Although another Cl^- enters the adsorbed-ion layer from the solution to compensate this loss, keeping the total amount of adsorbed Cl^- relatively constant, the entering Cl^- does not necessarily associate with the particular Ag^+ that has been uncovered.

In Fig. 12.4, the adsorbed Cl^- imparts a negative charge to the colloidal particle. Now, it is not possible to incur an appreciable separation of charge in a medium in which charges are free to move.* Because of this, positive Na^+ equal to the excess of Cl^- adsorbed must hover in the vicinity of the adsorbed-ion layer in a diffuse region called the *counter-ion layer*. Although the Na^+ counter ions are constrained to go wherever the charged colloidal particle goes, they are much more mobile and less tightly held than the adsorbed ions. The counter ions are held only electrostatically, with no chemical forces of attraction, in a rather diffuse layer. The charged colloidal particle and its counter ions are related to each other in the same way as the oppositely charged ions of a dissociable electrolyte.

The substance (AgCl in Fig. 12.4) that does the adsorbing is called the *adsorbent*; the adsorbed substance (NaCl) is called the *adsorbate*.†

The preceding explanation is limited to adsorption of electrolytes by ionic crystals. A similar mechanism suffices for adsorption of molecules by ionic precipitates (see Supplement, p. 719). However, adsorption upon a nonpolar substance, like charcoal, follows a different mechanism, which is beyond the scope of this text.

* To obtain even a minute separation of charge would require tremendous amounts of energy. An idea of the forces involved may be made clear by the following example. Suppose that 1 l of 1 *M* NaCl fills a cubical container, and that all the Na^+ (1 g) is crammed into one corner, while all the Cl^- (35 g) is crammed into the diametrically opposite vertex of the cube. It may be computed that the electrostatic force of attraction between the Na^+ and the Cl^- is about the same as the gravitational force of attraction between the earth and the sun (about 10^{24} g)! Ordinary amounts of work could not achieve such a separation to any appreciable extent.

† Although NaCl is called the adsorbate, it must be kept in mind that Na^+ and Cl^- are bound by different mechanisms. The Cl^- is primarily adsorbed and predominates in the adsorbed-ion layer. The Na^+ is "held" as a counter ion and is not adsorbed at all.

12C.3. Extent of Adsorption

Since adsorptive forces are chemical as well as physical, the extent of adsorption is dependent upon many properties of the adsorbent, the adsorbate, and the system containing them.

The dependence of adsorption upon these properties is given in the following sections. The generalizations that are made are for the most part empirical and rough working rules, based on only a few of the properties upon which adsorption depends. There are many exceptions. Further, each generalization applies to only one factor at a time, the others being assumed constant. As a consequence, contradictions may be encountered in attempts to apply several generalizations to a real case.

In spite of these exceptions and difficulties, however, the following statements and rules are often useful in explaining adsorption phenomena, and in suggesting how conditions should be altered to change the extent of a particular adsorption process.

12C.3a. Specific surface of the adsorbent. The *specific surface* of a substance is the surface presented by a unit weight of that substance, and is often expressed in square centimeters per gram. To illustrate how the specific surface increases as the subdivision of material increases, suppose that 1 g of a solid having a density of 1 g/cc exists as a single, cubic particle. This cube is then 1 cm on an edge, and the surface of the six sides is therefore $6 \times 1 \times 1 = 6 \text{ cm}^2$, which is the surface per gram, or the specific surface.

Now suppose that this 1-g cube is divided into smaller cubes, each having an edge of length L . Then the surface of each small cube is $6L^2$. Since the volume of each is L^3 , the number of such small cubes in 1 g (or 1 cc) is $1/L^3$. Hence the total surface of all such cubes in 1 g is $6L^2/L^3 = 6/L \text{ cm}^2$. Thus 1 cc of material subdivided into colloidal-sized cubes, with edges of length 0.01μ , or 10^{-6} cm , has a specific surface of $6 \times 10^6 \text{ cm}^2$, or about $\frac{1}{40}$ acre. This is a tremendously greater area than the 6 cm^2 of the original cube.

If the adsorbent particle is of appreciable size, most of the lattice ions are in the interior of the particle and cannot adsorb. The amount of adsorption per unit weight of adsorbent therefore does not even become appreciable until the specific surface becomes large, i.e., until the particle approaches colloidal dimensions. Furthermore, it is easy to see that not every surface ion of the crystal lattice can be covered with an adsorbed ion. Long before this state is reached, the repulsion between the like-charged adsorbed ions prevents further adsorption. In general, only a fraction of the surface ions is covered by adsorbed ions at any instant. For these reasons, the weight of adsorbed material is not often

more than a few per cent of the weight of adsorbent, even for a colloiddally dispersed adsorbent. Even so, this slight extent of adsorption is important in gravimetric analyses at the 0.1% error level, and in the separation of major constituents by precipitation, with the intention of recovering minor ones.

The nature of the surface and the extent of adsorption depend greatly upon the history of the adsorbent—its mode of precipitation, and whether it was digested, ignited, or otherwise aged. Generally, a given precipitate adsorbs less when formed slowly than when formed rapidly. As it ages, there is usually a decrease in adsorption, owing to a decrease in specific surface.

12C.3b. Concentration of adsorbate. For many electrolytes and nonelectrolytes in aqueous solution, the extent of adsorption is simply and empirically related to the concentration of the adsorbate by the *Freundlich* equation (M25)

$$\frac{m}{M} = kC^{1/n}$$

M is the weight of adsorbent, and m is the weight of the adsorbate; C is the equilibrium concentration of the adsorbed-ion species in solution. The constants k and n are described below.

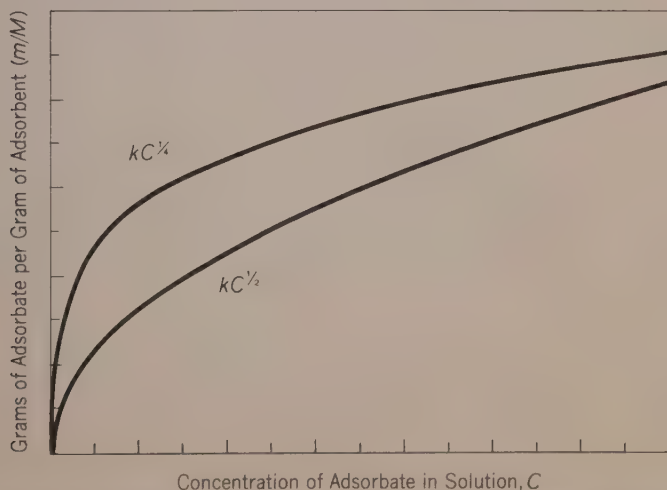


FIG. 12.5. Adsorption Isotherms Showing Dependence of Adsorption upon Concentration

Figure 12.5 shows typical plots of the Freundlich equation, one plot with a square-root dependence upon C and the other with a fourth-root dependence. Such plots are called *adsorption isotherms*, since the

Freundlich equation holds only at constant temperature. Figure 12.5 reveals that the adsorption process soon reaches a sort of saturation, where the amount adsorbed increases rather slowly as the concentration of adsorbable substance increases. It is reasonable to expect a limit to the amount adsorbed, when the surface is saturated with adsorbate and can hold no more. On the other hand, it may also be seen that the first traces of adsorbate may be held tenaciously, and may be very difficult to remove by washing. This latter property sometimes enables traces of substances to be efficiently removed from solution and concentrated upon the surface of an adsorbent; the operation of adsorption columns depends upon this principle.

The Freundlich equation describes the dependence of adsorption upon concentration within a particular system, when all other factors affecting adsorption are kept constant. When these other factors are changed, the magnitudes of k and n may change. The constant n is related to the nature of the chemical process occurring when the adsorbate passes from solution into the adsorbed layer, and usually lies between 1 and 5. The greater n is, the more efficient, relatively, is the adsorption at low concentrations. The magnitude of k describes the amount of adsorption. There are other adsorption equations that have a theoretical basis, and that fit a wider variety of isotherms than the Freundlich equation (p. 189). A comparison between the Freundlich and Langmuir isotherms is made in Prob. S20, page 698.

12C.3c. Chemical natures of adsorbate and adsorbent. If an adsorbable ion is such that it forms an undissociated or insoluble compound with the oppositely charged ion of the crystal lattice, this ion tends to be strongly adsorbed. The reasoning underlying this rule is that there are strong chemical forces between two such ions, and that these forces are favorable to adsorption. This rule was stated by Paneth and Fajans (W8). The following examples illustrate the use of this rule in predicting the nature of adsorption in specific cases.

Example 1. It follows directly from this rule that if a precipitate is formed in the presence of an excess of one of its lattice ions, the ion is adsorbed. Thus if AgCl is formed by adding AgNO_3 to an excess of NaCl , the potentially adsorbable ion species are Na^+ , Cl^- , and NO_3^- , as shown in Fig. 12.4. Since AgNO_3 and NaCl are much more soluble than AgCl , Cl^- is predominantly adsorbed, giving a negatively charged particle. Since Na^+ is the only positive ion in appreciable concentration, it must be the counter ion.

Example 2. In a manner similar to that in Ex. 1, it may be reasoned that a positively charged colloid will result if NaCl is added to an excess of AgNO_3 , Ag^+ being primarily adsorbed.

Example 3. A prediction may sometimes be made as to which of several kinds of ions will be predominantly adsorbed. Suppose that a solution contains the nitrates of

Fe^{3+} , Mg^{2+} , and Na^+ , each at 0.001 *M*. Suppose, further, that the Fe^{3+} is precipitated as $\text{Fe}(\text{OH})_3$ with a very slight excess of NaOH , so that the larger solubility product of $\text{Mg}(\text{OH})_2$ is not exceeded. Since $\text{Mg}(\text{OH})_2$ is more insoluble than NaOH , Mg^{2+} is adsorbed in preference to Na^+ . The counter ion is NO_3^- .

Example 4. Radioactive elements are often formed and used in such small amounts (10^{-10} – 10^{-15} g) that they cannot be precipitated and isolated alone from solution. Instead, they are coprecipitated or *carried* upon a finite, visible, and manipulable amount of a nonradioactive carrier precipitate. In order that the carrying may be efficient it is necessary that the carrier precipitate strongly adsorb the radio-element. Thus, traces of radio- Bi^{3+} are carried down well with BaCO_3 or $\text{Pb}(\text{OH})_2$, because $\text{Bi}_2(\text{CO}_3)_3$ and $\text{Bi}(\text{OH})_3$ are insoluble. On the other hand, radio- Bi^{3+} is not carried well with BaSO_4 or PbSO_4 in acid solutions, because $\text{Bi}_2(\text{SO}_4)_3$ is soluble in acid solutions (H1).

12C.3d. Presence of other adsorbable ions. The adsorption of a cation is increased by already adsorbed anions, and decreased by already adsorbed cations. A similar rule holds for adsorption of an anion. Hahn modified the Paneth-Fajans rule as follows: "A solute will be adsorbed by a precipitate if that precipitate already contains an adsorbed-ion layer opposite in sign to that of the solute ion, and if the solute ion forms an insoluble or undissociated compound with the oppositely charged adsorbed ion" (W8).

The adsorption of radio- Pb^{2+} upon CaSO_4 confirms this rule. When precipitated with excess H_2SO_4 from solutions containing a soluble Ca salt and traces** of radio- Pb^{2+} , SO_4^- is primarily adsorbed on the pre-

TABLE 12.2
ADSORPTION OF RADIO-PB BY CaSO_4 *

Precipitant Used to Form CaSO_4 †	Percentage of Total Radio-Pb ²⁺ That Is Carried on the CaSO_4
Tenfold excess of H_2SO_4	98.4
10% excess of H_2SO_4	92.2
5% excess of H_2SO_4	88.0
10% excess of CaCl_2	5.2
Sevenfold excess of CaCl_2	1.7

* Data taken from O. Hahn, *Applied Radiochemistry* (Ithaca, N.Y.: Cornell University Press, 1936), Table XVI, with permission of the publisher.

† Ca^{2+} or SO_4^{2-} precipitated with 85–100% efficiency in all cases, from alcoholic solution to repress the solubility of CaSO_4 .

cipitated CaSO_4 . Thus, the precipitate is negatively charged, and, further, the adsorbed SO_4^- forms an insoluble compound with Pb^{2+} , favoring adsorption of the latter, as shown in Table 12.2. If, however, solutions of a soluble sulfate with traces of radio- Pb^{2+} are precipitated

** Not sufficient to exceed the solubility product of PbSO_4 .

with excess CaCl_2 , the colloid formed is positively charged, owing to adsorption of Ca^{2+} . The Ca^{2+} is competitively and predominantly adsorbed over Pb^{2+} because of its higher concentration, and because CaSO_4 is a fairly insoluble substance. The positively charged colloid therefore does not have much tendency to adsorb radio- Pb^{2+} , as is also shown in Table 12.2. Thus if a precipitate is formed in the presence of an excess of one of its lattice ions, the excess ion is usually adsorbed to the exclusion of other ions of like sign, and may promote adsorption of other ions of opposite sign.

Example 5. Suppose, in Ex. 3, that the solution is buffered with an excess of 1 *M* NH_4NO_3 , in which the solubility product of $\text{Mg}(\text{OH})_2$ is not exceeded but that of $\text{Fe}(\text{OH})_3$ is. How would the extent of adsorption of Mg^{2+} on the $\text{Fe}(\text{OH})_3$ compare with that in Ex. 3? There is a tendency for NH_4^+ to be adsorbed as well as Mg^{2+} , since NH_4OH is a weak base. Owing to the relatively high concentration of NH_4^+ , it is adsorbed predominantly, giving a positively charged colloid. This is unfavorable to the adsorption of Mg^{2+} , which is therefore less than in Ex. 3. (This procedure is sometimes employed to displace an interfering adsorbate from a precipitate. In the gravimetric determination of Fe as Fe_2O_3 , any adsorbed Mg^{2+} causes error, but adsorbed NH_4^+ is volatilized on ignition, causing no error.)

Example 6. If a precipitate is formed in acidic or basic solution, the adsorption of H_3O^+ or OH^- must always be considered, since these ions are readily adsorbed and often exert a profound effect upon the adsorption of other ions that may be present. For example, $\text{Fe}(\text{OH})_3$, formed in basic solution by addition of excess base to Fe^{3+} , has a high tendency to adsorb OH^- and to become negatively charged, promoting adsorption of metallic ions such as Ba^{2+} . The Ba^{2+} adsorbed in this way may be greatly reduced by forming the $\text{Fe}(\text{OH})_3$ at low *pH*, which decreases the adsorbed OH^- and therefore also decreases the adsorbed Ba^{2+} (w2).

12C.3e. Other factors affecting the extent of adsorption

Temperature. Heat is usually given off in the adsorption process, and the extent of adsorption decreases with increasing temperature. Hence, if possible, a precipitation is carried out at elevated temperature in order to minimize adsorption.

Solvent. The intermolecular forces between a given adsorbent and a given adsorbate are greatly altered by a change in solvent, and so is the extent of adsorption. There are no simple rules that predict the effect of solvent nature on adsorption.

Charge on the adsorbable ion. In general, other conditions being equal, ions of higher charge are adsorbed more readily than ions of lower charge. This is the Schulze-Hardy rule, and is of subordinate importance to the Paneth-Fajans-Hahn rules. As an example, BaSO_4 adsorbs La^{3+} more strongly than Mg^{2+} , which in turn is adsorbed more strongly than Na^+ .

Size, shape, and deformability of the adsorbed ion. Small or deformable ions often fit into the surface layer more readily than large, rigid ones.

Thus the adsorbability of member ions of the same group in the periodic table is often related to ionic radius. For example, Cl^- is adsorbed by BaSO_4 more strongly than Br^- , which in turn is adsorbed more strongly than I^- (w8).

12C.4. Stability of Colloids

12C.4a. Stabilization. There are factors which tend to make the colloidal state unstable. The particles are inclined to settle under the influence of gravity, and to separate from solution. Also, there is a tendency for colloidal particles to coalesce to larger particles with less surface and lower surface energy. These tendencies, however, are more than offset by others that contribute to the stability of the colloidal state.

The large specific surface of the small particles offers great resistance to motion, and the rate of settling is negligible. Furthermore, the size and the mass are so small that bombardment by solvent molecules keeps the colloidal particle in constant motion (i.e., Brownian motion).

In *hydrophobic* colloids, sometimes called *sols*, there is little intermolecular attractive force between the dispersed phase and water. There is also little tendency for hydration of the colloidal particles, which form as small crystals or aggregates. Such colloidal particles are stabilized by their charges, acquired by adsorption. The like-charged colloidal particles repel each other, reducing the collisions that cause coalescence. Elements, oxides, and salts (which include most gravimetric precipitates) often form hydrophobic colloids.

In *hydrophilic* colloids, sometimes called *gels*, there is much intermolecular attractive force between the colloidal phase and water. The colloidal particles form in flocs or jellies containing much water in and around the particles. Such particles may, of course, be rendered stable by acquisition of charge, just as are hydrophobic particles. But even in the absence of a charge, hydrophilic colloidal particles are stabilized by the surrounding layer of solvent molecules, which prevents contact and coalescence upon collision. Proteins, higher carbohydrates, and soaps often form gels.

Whether a colloidal particle is hydrophobic or hydrophilic depends on the nature of the molecules that are exposed to the solution. Polar or ionizable groups that can coordinate with water render the colloid hydrophilic, while nonpolar groups render a colloid hydrophobic. A colloid may sometimes be changed from hydrophobic to hydrophilic, or vice versa, simply by adsorption or desorption to change the nature of the adsorbed layer.

A hydrophobic colloid may be made hydrophilic and stabilized by a protective layer of a hydrophilic colloid surrounding each particle. This

layer prevents coalescence of the enclosed hydrophobic particle upon collision. Hydrophobic colloids, formed in the presence of hydrophilic colloids (such as gelatin, gum arabic, or starch) often acquire such a stabilizing layer. Thus stable colloidal solutions of silver halides may be obtained in the presence of gelatin. In the titration of chloride with standard AgNO_3 and an adsorption indicator, dextrin is used to keep the AgCl in the colloidal state.

12C.4b. Coagulation. To obtain a filterable precipitate it is sometimes necessary to coagulate a colloid. The mechanism of coagulation is described in the Supplement (p. 720). Practical methods of coagulation are: (1) *Digestion*. The coagulation process requires time, just as does the growth of crystals. (2) *Temperature Changes*. In general, the rate of coagulation increases as temperature increases. The effect of changing temperature is very complicated; not only is the extent of adsorption of the stabilizing ions affected, but so are the other factors upon which adsorption depends. Some gels decrease in stability with a decrease in temperature. (3) *Stirring or Agitation*. Mechanical stirring, agitation, or shock increase the rate of coagulation by increasing the opportunity for collision among the colloidal particles. (4) *Electrolytes*. Small amounts of added electrolytes may coagulate hydrophobic sols by neutralizing the stabilizing charge. Electrolytes are not so effective for coagulating gels. (5) *Miscellaneous Methods*. Coagulation is sometimes brought about by radiation, by electric fields, or by ultrasonic fields. Stabilizing agents may sometimes be removed by chemical destruction or by dialysis,* with resulting coagulation of the colloid.

12C.4c. Peptization. Coagulated hydrophilic systems may often be redispersed simply by reversing the conditions that cause coagulation. Thus gelatin and soap gels that have been coagulated by cooling may be reconverted to colloids by warming. However, if a chemical change accompanies the coagulation (as of egg albumen by heating), the change may be irreversible.

When hydrophobic colloids are coagulated the process is not often reversible, especially if the coagulum is allowed to age or to dry out, so that the particles are cemented together. Occasionally, a freshly coagulated hydrophobic colloid may be peptized by washing out the coagulating electrolyte. This may happen in the gravimetric determination of chloride as AgCl .

* In dialysis, the colloidal solution is placed in contact with a wash liquid through a semipermeable membrane whose pores are too small to pass the colloidal particles, but large enough to pass soluble electrolytes. The stabilizing electrolyte may thus be lost to the wash solution, leaving behind only the colloidal particles, which will coagulate if the washing is carried far enough.

12D. CONTAMINATION OF PRECIPITATES

12D.1. Types of Contamination

Contamination is the carrying along of any other substances by a sought-for precipitate. Contaminants may be divided into two classes, according to the mechanisms by which they associate with the sought-for substance. Sometimes impurities are precipitated with the sought-for precipitate simply because the solubility limits of the impurity compounds are exceeded; this is called *contamination by true precipitation*, for want of a better name. On the other hand, *coprecipitation* or *carrying* refers to the contamination of a sought-for precipitate by substances that are normally soluble under the conditions of the precipitation, and that would not be expected to precipitate with the sought-for substance.

The following example contrasts these two types of contamination. Suppose that a solution contains Fe^{3+} , Al^{3+} , Mg^{2+} , and Na^+ , all as nitrates. Suppose, furthermore, that the basicity is adjusted by buffering to give a hydroxyl-ion concentration sufficient to exceed the small solubility products of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$, but not that of the more soluble $\text{Mg}(\text{OH})_2$. The precipitate formed is a mixture of $\text{Fe}(\text{OH})_3$ and $\text{Al}(\text{OH})_3$. The $\text{Al}(\text{OH})_3$ is not coprecipitated with the $\text{Fe}(\text{OH})_3$, or vice versa; these substances are both truly precipitated, since their solubility products are exceeded, and nothing else would be expected. On the other hand, if the $\text{Fe}(\text{OH})_3$ - $\text{Al}(\text{OH})_3$ precipitate is found still to contain Mg^{2+} or Na^+ after washing to remove the mother liquor, these substances are said to be "coprecipitated," because they form no insoluble compounds under the conditions of precipitation.

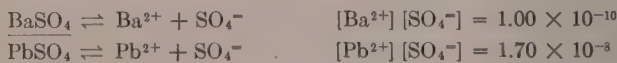
12D.1a. Contamination by true precipitation

Simultaneous precipitation. All substances whose solubilities are exceeded precipitate along with the sought-for (host) compound. The simultaneous precipitation of $\text{Al}(\text{OH})_3$ and $\text{Fe}(\text{OH})_3$ described above is an example. If the impurity compound is dissimilar to the host, so that both substances crystallize independently, then the solubility-product relationships hold, and solution and precipitate compositions may be calculated as shown in the two following illustrative examples.

On the other hand, if mixed crystals or double compounds form (i.e., if the impurity compound is soluble in the sought-for compound, or vice versa), the solution is not saturated with the pure compounds, and the solubility-product relationships do not hold. There may then be coprecipitation of the impurity with the host long before the solubility product of the impurity compound is exceeded. Double compound formation is discussed in the Supplement (p. 723). Mixed crystal formation is described under isomorphic coprecipitation (p. 199).

Example 1. A 100.0-ml portion of a solution contains 0.01000 *M* each of $\text{Ba}(\text{NO}_3)_2$ and $\text{Pb}(\text{NO}_3)_2$. In an attempt to prepare pure BaSO_4 , a worker adds a slight excess of SO_4^{2-} (over the Ba^{2+}) by adding 101.0 ml of 0.01000 *M* H_2SO_4 . Assuming that the solubility-product principle holds, and that H^+ does not complex SO_4^{2-} , calculate the composition of the final solution and precipitate.

Since the SO_4^{2-} is in excess of the Ba^{2+} , and since PbSO_4 is quite insoluble, the solution will probably be saturated with respect to both substances.



So far, there are two equations in three unknowns. The remaining equation may be obtained by realizing that a good concentration of Pb^{2+} is left in solution, and that the SO_4^{2-} must therefore be very low—in other words, the SO_4^{2-} added is quantitatively precipitated.* In this case,

$$[\text{Ba}^{2+}] + [\text{Pb}^{2+}] = \frac{\left(\begin{array}{c} \text{mmoles Ba}^{2+} \text{ and Pb}^{2+} \\ \text{originally present} \end{array} \right) - \left(\begin{array}{c} \text{mmoles SO}_4^{2-} \\ \text{added} \end{array} \right)}{(\text{total ml of solution})}$$

$$[\text{Ba}^{2+}] + [\text{Pb}^{2+}] = \frac{(100.0)(0.01000) + (100.0)(0.01000) - (101.0)(0.01000)}{201.0}$$

Solution of these three equations gives

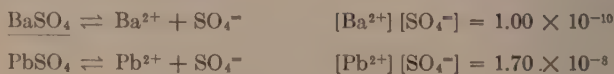
$$\begin{aligned} [\text{Pb}^{2+}] &= 0.00490 \text{ M} \\ [\text{Ba}^{2+}] &= 2.88 \times 10^{-5} \text{ M} \\ [\text{SO}_4^{2-}] &= 3.47 \times 10^{-6} \text{ M} \end{aligned}$$

The composition of the precipitate obtained can also be found.

$$\begin{aligned} \left(\begin{array}{c} \text{mmoles BaSO}_4 \\ \text{pptd.} \end{array} \right) &= \underset{\substack{\uparrow \\ \text{Total Ba}^{2+}}}{(100.0)(0.01000)} - \underset{\substack{\uparrow \\ \text{Ba}^{2+} \text{ in soln.}}}{(201.0)(2.88 \times 10^{-5})} = 0.994 \\ \left(\begin{array}{c} \text{mmoles PbSO}_4 \\ \text{pptd.} \end{array} \right) &= (100.0)(0.01000) - (201.0)(0.00490) = 0.015 \end{aligned}$$

The precipitate therefore contains 0.015 moles PbSO_4 per mole of BaSO_4 .

Example 2. In another attempt to prepare pure BaSO_4 from the solution of Ex. 1, the worker decides to add only 98.0 ml of 0.01000 *M* H_2SO_4 . With the assumptions of Ex. 1, calculate the composition of the solution at equilibrium, and show that the precipitate is indeed pure BaSO_4 .



Since the BaSO_4 is much less soluble than PbSO_4 , and since the SO_4^{2-} added is less than equivalent to the Ba^{2+} , the chances are that PbSO_4 will not precipitate. Mak-

* To obtain the third equation, the assumption could also be made that the Ba^{2+} left in solution is negligible compared to the Pb^{2+} , since BaSO_4 is much more insoluble than PbSO_4 . This assumption is valid and gives the same answers as above.

ing this assumption will permit an easy solution to the problem, and once the answers are obtained, the assumption may be tested.

Since no PbSO_4 is formed, the added SO_4^{2-} will almost quantitatively precipitate an equivalent amount of Ba^{2+} , and the concentration of Ba^{2+} left in solution may be calculated

$$[\text{Ba}^{2+}] = \frac{\left(\begin{array}{c} \text{mmoles Ba}^{2+} \text{ origi-} \\ \text{nally present} \end{array} \right) - \left(\begin{array}{c} \text{mmoles SO}_4^{2-} \\ \text{added} \end{array} \right)}{(\text{total ml of solution})}$$

$$[\text{Ba}^{2+}] = \frac{(100.0)(0.01000) - (98.0)(0.01000)}{198.0} = 1.0 \times 10^{-4} M$$

The $[\text{SO}_4^{2-}]$ in the saturated solution of BaSO_4 may now be calculated:

$$[\text{SO}_4^{2-}] = \frac{1.00 \times 10^{-10}}{[\text{Ba}^{2+}]} = \frac{1.00 \times 10^{-10}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-6} M$$

The highest $[\text{Pb}^{2+}]$ that could exist in this solution without precipitation of PbSO_4 is

$$[\text{Pb}^{2+}]_{\text{max}} = \frac{1.70 \times 10^{-8}}{[\text{SO}_4^{2-}]} = \frac{1.70 \times 10^{-8}}{1.0 \times 10^{-6}} = 0.017 M$$

On the other hand, the $[\text{Pb}^{2+}]$ that actually exists in the final solution is much less than this maximum value.

$$[\text{Pb}^{2+}] = 0.01000 \times \frac{100.0}{198.0} = 0.0050 M$$

There is therefore no precipitation of PbSO_4 , and the precipitate is pure BaSO_4 , which is consistent with the original assumption.

At this point, the student may ask, "What would be the nature of my answer if I had assumed, as in Ex. 1, that there was some precipitation of PbSO_4 ?" Such an (erroneous) assumption might easily be made, and an answer obtained. On testing the answer, however, it will be found inconsistent with the assumption. The nature of the inconsistency will lead logically to the correct assumption, and a second try at the problem may be made.

The most effective way to deal with contamination by simultaneous precipitation is to adjust conditions so that the solubilities of the impurity compounds are not exceeded. This may require removal of the impurities before precipitation, either by actual separation or by complexing. If such removal of impurities is not feasible, a more selective precipitant may be tried. The common methods of washing, digestion, and reprecipitation are seldom effective.

Postprecipitation. The oxalates of both Mg and Ca are insoluble, but pure CaC_2O_4 may be precipitated from mixtures of Ca and Mg salts, even under conditions for which the solubility product of MgC_2O_4 is exceeded. MgC_2O_4 has a great tendency to form supersaturated solutions, whereas CaC_2O_4 has not. Solutions of MgC_2O_4 with high degrees of supersaturation may remain stable for days, and, even after crystalliza-

tion begins, equilibrium is reached only slowly. CaC_2O_4 precipitates and reaches equilibrium more rapidly. The precipitation of CaC_2O_4 in the presence of MgC_2O_4 is therefore not based on any great difference in solubilities, but rather on a difference in rates of crystallization. In mixtures, however, the CaC_2O_4 precipitate acts as seeds for the MgC_2O_4 , and hastens precipitation of the latter. Thus if the CaC_2O_4 precipitate is left in contact with the mother liquor containing MgC_2O_4 , the latter soon precipitates out upon the surface of the CaC_2O_4 , as may be shown by microscopic examination of the precipitate.

This type of contamination is called *postprecipitation*, and is easily recognized, for it is increased by digestion, rather than decreased like coprecipitation. Postprecipitation may be reduced by allowing the mother liquor to remain in contact with the desired precipitate no longer than is necessary for its complete precipitation. If only a small proportion of the impurity is carried with the first precipitate, reprecipitation

TABLE 12.3*
POSTPRECIPITATION OF ZnS ON Bi_2S_3 †

HCl Molarity of the Original Solution	Time of Precipitation (Minutes)	Per Cent of Total Zn in the Bi_2S_3 Precipitate
0.15.....	5	30
	15	75
	60	90
	60	2‡
0.20.....	5	0.5
	15	31
	60	82
	60	0.5‡
0.25.....	5	0
	15	2
	60	32
0.30.....	60	2
	180	7

* Data taken from I. M. Kolthoff and F. S. Griffith, *Journal of Physical Chemistry*, 42, 531 (1938), Table 1, with permission of the copyright owners, The Williams & Wilkins Company.

† Original solution contained 0.025 *M* BiCl_3 , 0.025 *M* ZnCl_2 , and HCl. H_2S was passed steadily through the agitated solution for the specified time. After this time, the precipitate was removed and the supernate analyzed for Zn.

‡ Blank. No Bi present.

is helpful in reducing such contamination. The extent of postprecipitation depends primarily upon those conditions which affect the rate of precipitation; and therefore the extent is usually reproducible only when the conditions are critically controlled. Conversely, the extent may sometimes be greatly influenced by a change in conditions.

Postprecipitation is not rare; it may be at least partly responsible for the contamination of the acid-insoluble Cu-group sulfides when precipitated in acid solution in the presence of certain members of the acid-soluble Zn group. Table 12.3 shows that no appreciable ZnS forms in acid solution in the absence of Bi_2S_3 ; but in the presence of Bi_2S_3 the Zn content of the precipitate increases with time. The amount of Zn precipitated is highly dependent on the acidity. The effect of other conditions may be found in the original article (K14).

12D.1b. Contamination by coprecipitation. Coprecipitation on ionic precipitates occurs through adsorption. One ion of the impurity compound is absorbed on the precipitate. Then, when the precipitate is isolated from the mother liquor, the counter ion goes along with the adsorbed ion to form the impurity compound. However, the way in which the impurity is actually deposited in the host crystal depends upon the structural and chemical similarity between the host and impurity compounds, and may differ considerably for different pairs of compounds. The different "types" of coprecipitation are discussed below on this basis, much after the manner of Buckley (B28). The demarcation among types is not sharp, and, furthermore, any real case of coprecipitation may involve more than one of the following types.

The impurity is isomorphic and miscible with the host. Two compounds are said to be *isomorphic* if they possess the same type of formula and the same type of crystal structure. If in addition the crystal lattice spacings are about the same (within 10–15%), the host crystal may incorporate large amounts of the isomorphic impurity with little or no distortion; as a result the two compounds may form mixed crystals and may be miscible in all proportions. The distortion decreases as the magnitudes of the lattice spacings of the two compounds approach one another. Thus NaCl, KCl, KBr, and KI are all isomorphic, crystallizing in the cubic system, with atom-pair spacings of 5.63, 6.26, 6.59, and 7.10×10^{-8} cm, respectively. These spacings explain why KCl forms good mixed crystals with KBr, but less perfect ones with NaCl and KI. However, similar lattice spacing is not sufficient; for mixed crystals to be formed the type of bonding must also be similar. Thus KCl (a univalent salt with ionic bonding) does not form mixed crystals with PbS, which also crystallizes in the cubic system with a spacing of 5.97×10^{-8} cm, because PbS is a bi-bivalent salt with considerable covalent bonding.

The impurity is distributed throughout the host crystal, sometimes quite uniformly, as in Fig. 12.6a, and sometimes nonuniformly, as in Fig. 12.6b. (The factors affecting distribution are examined in the Supplement, p. 724.) For example, BaSO_4 and PbSO_4 are isomorphic. If SO_4^{2-} is added to a solution containing Ba^{2+} and traces of Pb^{2+} in con-

centrations not sufficient to exceed the solubility product of PbSO_4 , BaSO_4 is precipitated and Pb^{2+} is adsorbed upon the surface of the first fine microcrystals formed. Were the Pb^{2+} a nonisomorphic impurity, it would be displaced from the BaSO_4 surface as the crystals grow, so that perfect layers of Ba^{2+} and $\text{SO}_4^{=}$ would be built up. However, since

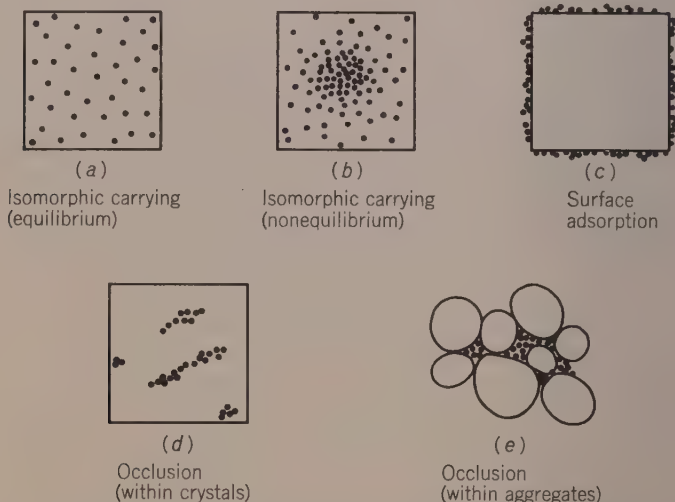


FIG. 12.6. Distribution of Coprecipitated Impurities—Coprecipitated impurities are indicated by dots.

PbSO_4 is isomorphic, impure BaSO_4 crystals may readily grow without appreciable distortion, with Pb^{2+} randomly occupying lattice positions that are normally occupied by Ba^{2+} in a pure crystal. The isomorphic Pb impurity may thus be distributed throughout the almost perfectly formed BaSO_4 crystals.

Isomorphic contamination is very troublesome, because it cannot be appreciably diminished by the ordinary methods for reducing coprecipitation. In general, isomorphic coprecipitation should be suspected as predominant whenever a rather high fraction (10–100%) of the total precipitable impurity is carried, and when this cannot be reduced significantly by the methods of Sec. 12D.2 (p. 202). The only really effective way to reduce isomorphic contamination is to remove the impurity before precipitating the host compound. Such removal is often difficult, for isomorphic compounds are usually similar in chemical behavior also.

The impurity is soluble in the host. When two substances are not so similar as to be miscible in all proportions, they may still be soluble to some extent in each other. Such may be the case when two compounds have the same crystal form but considerably different lattice spacings

—for example, KH_2PO_4 and $(\text{NH}_4)_2\text{H}_2\text{PO}_4$, both monoclinic crystals. Even for substances crystallizing in different systems, one substance may tolerate limited amounts of the other without sufficient distortion to lose its characteristic crystal symmetry and structure. In small amounts, the impurities may be distributed throughout the host in a manner similar to isomorphic impurities. In larger amounts, such impurities may be sufficient to cause distortion and flaws in the host crystal. $\text{Ba}(\text{NO}_3)_2$, KNO_3 , and other alkali salts seem to be carried in this way by BaSO_4 (F4, W4).

The impurity is adsorbed on the surface of the host. A contaminating ion may be adsorbed upon a precipitate, and when the precipitate is separated from the mother liquor not only the adsorbed ion goes along, but so does the counter ion. As shown in Fig. 12.6c, the impurity is distributed over the particle surfaces of the precipitate.

Coprecipitation by surface adsorption is important only for precipitates with large specific surface, such as the gelatinous, hydrous oxides; it is seldom important for coarsely crystalline precipitates or aggregates. Where surface adsorption is the predominant mechanism, the bulk of impurity may be removed by simple washing. Sometimes the last traces of impurity may be held tenaciously, and may remain even after extended washing. The nature and extent of the coprecipitation follow approximately the adsorption rules. Although the amount of surface-adsorbed impurity is describable by the Freundlich equation, the converse of this statement is not always true. That is, there are cases of contamination by mechanisms other than adsorption (such as occlusion) that sometimes fit the empirical Freundlich equation.

The impurity is occluded by the host. An adsorbed, nonisomorphic impurity never fits as well into a crystal structure as the host substance itself. Hence even though an impurity may be temporarily adsorbed on the surface of a crystal, it tends to be pushed out and replaced by the host substance as the crystal grows, so that the interior of the crystal is uncontaminated, the impurity being restricted only to the surface of the particle. However, if the crystal grows so rapidly that the impurity does not have time to be desorbed, it may be covered over and entrapped within the rapidly growing crystal. Such enclosed impurities are said to be “occluded” or “internally adsorbed.” Impurities occluded in this way differ in several important respects from isomorphically carried ones: (1) The extent of occlusion may not follow any particular rules, but may be exceedingly variable and highly dependent upon the mode of formation of the precipitate. (2) The occluded impurity may be discontinuously distributed throughout the precipitate, along flaws and imperfections in the precipitate wherever they are present (Fig. 12.6d). (3) It is possible to remove the occluded impurity by washing if the wash

liquid can reach it. Hence digestion and reprecipitation are often effective in removing occluded impurities.

In another mode of occlusion, impurities are entrapped in the spaces between the particles in aggregates (Fig. 12.6e). These voids may trap not only impurities adsorbed on the surfaces of the void, but also mother liquor with its impurities, whether they are adsorbable or not.

12D.2. Reduction of Contamination

Generally there is no visible evidence of contamination, and its existence may only be suspected if a gravimetric analysis is in error. Sometimes the mechanism of contamination may be deduced from the magnitude of the error and its variation with changing experimental conditions, whereupon measures may be taken to diminish the error.

Methods of preventing or reducing contamination were named under the various types of contamination. In this section these methods are described in greater detail. Table 12.4 summarizes the kinds of contamination that may be significantly diminished by each of the methods.

TABLE 12.4

SUMMARY OF METHODS FOR REDUCING CONTAMINATION OF PRECIPITATES

METHOD	TYPES OF CONTAMINATION THAT MAY USUALLY BE DIMINISHED BY THE METHOD*				
	Simultaneous Precipitation	Post-precipitation	Isomorphism or Solubility in the Host	Surface Adsorption	Occlusion
Washing.....				✓	
Maintenance of low degree of supersaturation.....	?			✓	✓
Digestion.....	?			✓	✓
Reprecipitation.....	?	?	?	✓	✓
Elimination of contaminant.....	✓	✓	✓	✓	✓

* A question mark indicates that the method may be effective in some cases.

12D.2a. Washing. Washing serves to remove surface-adsorbed impurities and impurities in the mother liquor held mechanically by the precipitate. Simple washing is quite ineffective for other kinds of contamination. The considerations in the choice of a wash liquid are many,

and have been discussed previously. (1) The solubility of the sought-for precipitate in the wash liquid should be low. (2) The wash liquid should not peptize the precipitate. (3) The wash liquid should neither metathesize the sought-for precipitate nor cause further precipitation of impurities. For example, MgNH_4PO_4 tends to hydrolyze to MgHPO_4 when washed with water, and must be washed with dilute NH_3 to prevent such hydrolysis. Hydrolyzable metal salts, such as those of Fe^{3+} and Al^{3+} , cannot simply be washed away from a sought-for precipitate with water, for they hydrolyze and contaminate the precipitate (p. 769). Dilute acid may be used to prevent such hydrolysis.

12D.2b. Maintenance of a low degree of supersaturation. Large perfect crystals have the best opportunity to form, and surface adsorption and occlusion are reduced to a minimum, when precipitates are formed (1) in dilute solution, (2) with good stirring, (3) with slow addition of reagents, and (4) at high temperatures. Each one of these four measures is neither always effective nor always convenient, but they are each "standard technique" for reducing surface-adsorbed and occluded impurities. Also, when the contaminant compound is deposited because its solubility is temporarily exceeded in the precipitation process, these measures may sometimes reduce such contamination.

12D.2c. Digestion. In digestion, a precipitate is allowed to stand in contact with its mother liquor for a considerable time. During this time the precipitation and coagulation processes reach equilibrium. Digestion may give purer and more filterable precipitates in several ways.

1. Small crystals develop into larger ones with less surface area (see Supplement, p. 727). Impurities held by the small particles are liberated into the mother liquor during this process, which is called *Ostwald ripening*.

2. Perfection of individual crystals occurs. Adsorption or occlusion of nonisomorphic impurities gives rise to strain, distortion, and flaws in the host crystal. By spontaneous rearrangement, these imperfect regions tend to become identical with the more ordered host structure, in which process the impurities are extruded. Experiments have shown that an imperfect, strained region of a crystal is more soluble than a perfect region. Hence imperfect regions near the surface slowly disappear, liberating their impurities to the mother liquor, and the perfect regions grow during digestion. This rearrangement may also occur within the interior of the crystal, without the aid of the solvent medium; the impurities are forced along minute imperfections and cracks to the surface, where they are lost. The healing out of flaws and imperfections has been shown directly and indirectly (J1, K17). The process of rearrangement may occur without any apparent increase in particle size, and may

be more important in elimination of impurities than Ostwald ripening. Rearrangement of this sort usually requires considerable time, and may not take place appreciably in a short digestion process.

3. The stable form of the precipitates is attained. Often, the precipitate that is first formed may be an allotropic modification of the sought-for precipitate. Such forms are often amorphous, and consequently impure or unfilterable. Being less stable, however, they have higher solubilities than the stable form, and they may recrystallize to the stable form during digestion. In the recrystallization, impurities are returned to the mother liquor, and the stable form is usually purer.

4. An equilibrium is reached with respect to adsorbed impurities, in which harmful impurities adsorbed preponderantly at the beginning of the precipitation process may be returned to the mother liquor or replaced with less harmful ones. For example, in the gravimetric determination of NaCl as AgCl, the Cl^- is precipitated by adding AgNO_3 to the NaCl solution. At the beginning, when chloride is in large excess, coprecipitation of NaCl is high. Even if such coprecipitated NaCl were not removed by washing, the result would still be low, since calculations are based on the assumption that all Cl^- forms AgCl. However, the coprecipitated NaCl is metathesized during digestion to AgCl, after addition of excess AgNO_3 , and no error results. (During digestion, in the presence of excess AgNO_3 , AgNO_3 is coprecipitated. This does not make results high, however, since washing later removes this impurity.)

5. If a contaminant compound is formed because its solubility is temporarily exceeded during the precipitation process, digestion sometimes allows such a contaminant to redissolve.

From the nature of these changes, it may readily be seen that the extent and even the nature of contamination may be profoundly changed by digestion, no matter by what mechanism the contamination occurs.

Digestions are sometimes carried out at elevated temperatures, to speed the processes that occur, and to reduce the time required.

However, digestion does not serve to decrease all types of contamination. Digestion should never be allowed where postprecipitation is a possibility. Contamination by simultaneous precipitation and isomorphic carrying may be increased or decreased by digestion, but not often significantly so. If the precipitate (e.g., a gelatinous precipitate) is one whose specific surface does not decrease in digestion, digestion may be of little use in decreasing contamination by surface adsorption.

12D.2d. Reprecipitation. In a reprecipitation a sought-for precipitate is washed, redissolved in a pure solution, and reprecipitated. If the impurities are inefficiently carried, the quantities present at the repre-

cipitation are much smaller than at the first precipitation, and the second precipitate is consequently much purer. This method is therefore satisfactory in decreasing surface-adsorbed and occluded impurities. It may also be good for reducing contamination by postprecipitation, if only a fraction of the postprecipitable impurities come down.

Reprecipitation is unsatisfactory whenever a large proportion of an impurity goes with the sought-for precipitate, for then the amount of impurity will be almost as great in the second precipitation as in the first. Thus reprecipitation may be of little avail in dealing with contaminants carried by simultaneous precipitation or isomorphically, where the carrying efficiency is usually high. Reprecipitation is also unsatisfactory whenever the contamination arises from a reagent itself, or from the precipitation process itself. Thus contamination of hydroxides with basic salts formed during the precipitation process cannot be greatly reduced just by reprecipitation.

Because of the extra time required, and because the extra manipulation increases the probability of error, reprecipitation is not generally desirable. In general, reprecipitation is only used for precipitates that are extremely easy to redissolve. In some cases where it might be desirable it cannot be used because there are no simple methods of solution (e.g., BaSO_4).

12D.2e. Elimination of the contaminant. When none of the preceding methods is easily applicable or effective in reducing contamination, the last resort is to eliminate the contaminant. This may be done in either of two ways. (1) The contaminant may actually be separated and removed from the sought-for substance before precipitation. Such separations may be troublesome, especially if the contaminant and sought-for substances are chemically similar. (2) The contaminant may be changed chemically to a less objectionable form, without actual separation from the sought-for substance. Complexing or redox reactions are sometimes employed. For example, in the BaSO_4 determination, Fe^{2+} is adsorbed much less than Fe^{3+} , and considerably higher concentrations of Fe^{2+} than of Fe^{3+} are tolerable. Interference of Fe^{3+} may be greatly diminished by reducing it to Fe^{2+} before precipitation of the BaSO_4 .

Care must constantly be exercised to keep contaminants out of the analytical process. The analytical steps that precede the precipitation often involve much chemistry. In these steps, the analyst must be constantly on the watch not only for opportunity to remove interferences but also to avoid reagents that will coprecipitate or otherwise interfere later. Indiscriminate use of reagents in the first parts of the analytical process, without view toward the later steps, can cause great loss of time and effort.

12D.3. Sign of the Contamination Error

If the contaminant compound in the precipitate does not contain the sought-for substance, the weight of precipitate obtained is too high and the error is positive. However, the error due to contamination is not always positive. If the contaminant is a compound containing the sought-for substance, but different from the sought-for compound, the error may be positive or negative, depending on whether the equivalent weight of the impurity compound is greater or less than that of the sought-for compound. An example lies in the coprecipitation of NaCl with AgCl in the determination of chloride (p. 204). Another example is given below. Generally, a critical consideration of the behavior of the impurity compound through the whole course of an analysis is necessary in order to decide whether the error is positive, negative, or insignificant. For example, an impurity compound may be volatilized on ignition, and may cause no error in the determination.

Example. If, in the determination of Na_2SO_4 , the solution of BaCl_2 precipitant is slowly added to the solution of Na_2SO_4 , the BaSO_4 precipitate is contaminated with occluded Na_2SO_4 . This is particularly true of the first portions of precipitate formed, since the concentration of Na_2SO_4 is then a maximum. Part of the sulfate is therefore combined with 2Na instead of Ba, and the resulting precipitate has an erroneously low weight. If acid is present in the precipitation process this negative error is aggravated, for H_2SO_4 is also coprecipitated, and this is entirely lost by volatilization on ignition of the precipitate.

QUESTIONS

Sections 12A, B

1. Is it possible to arrange the desirable properties of a precipitate in order of importance?
2. Consider any specific gravimetric method with known conditions of performance. Give an example of how a change in one of these conditions might achieve a fuller realization of one of the desirable properties, but might also adversely affect other equally desirable properties.
3. Fe may be determined gravimetrically as Fe_2O_3 and Ag may be determined as AgCl. Discuss the relative selectivities of these two methods.
4. Are all precipitates easy to dry? Explain how certain attempts to dry a precipitate completely may render it unfit for gravimetric analysis.
5. Explain what happens when the solution represented by point *a* in Fig. 12.2 (p. 180) is evaporated at constant temperature.
6. Delineate the metastable region for nucleus formation on Fig. 12.3 (p. 181). Is this region metastable also with respect to growth of crystals?
7. Explain the following statements with the help of Fig. 12.3. (a) In a practical precipitation process, all nucleation occurs very early, and only growth occurs thereafter. (b) The number of particles and the final size are determined during the nucleation period.

8. A precipitate tends to form as colloidal aggregates. Describe generally what measures might be used to increase the crystallinity of the aggregates.

9. Describe the difficulties that might be encountered in filtering a gelatinous precipitate. Describe techniques that may be used to remedy these difficulties.

10. In filtering a finely crystalline precipitate through paper, a small part of the precipitate runs through. Describe techniques that might be tried to reduce such losses.

11. When BaCrO_4 is precipitated by mixing BaCl_2 and Na_2CrO_4 solutions, the particles are very fine. List techniques that might increase the particle size.

Section 12C

1. Are the following systems homogeneous or heterogeneous when equilibrium is reached? Give the number of phases at equilibrium, and give the components. (a) 50 ml benzene plus 60 ml H_2O . (b) 20 g CaCO_3 plus 200 ml H_2O . (c) 2 g NaCl plus 100 ml H_2O . (d) 50 ml 0.20 M NaNO_3 plus 80 ml 0.10 M KCl . (e) 60 ml 0.10 M NaCl plus 80 ml 0.10 M AgNO_3 . (f) 100 ml 0.10 M NaOH plus 50 ml 0.20 M HCl .

2. Why are the counter ions not attracted right into the adsorbed-ion layer by the oppositely charged adsorbed ions?

3. PbCrO_4 forms a colloidal suspension in excess Na_2CrO_4 . What is the charge on the colloid? How might it be coagulated?

4. Speculate as to what solute species is primarily adsorbed, and predict the charge on the particles of precipitate, for each of the following precipitates: (a) CaSO_4 , formed by adding H_2SO_4 to excess CaCl_2 . (b) CaSO_4 , formed by adding CaCl_2 to excess H_2SO_4 . (c) $\text{Fe}(\text{OH})_3$, formed by adding FeCl_3 to excess NaOH .

5. The adsorption process is spoken of as an equilibrium process. In practice, what phenomena might operate to make it seem not to be so?

6. The dyes wool violet and methylene blue are adsorbed more highly by AgBr in a solution containing excess AgNO_3 than in a solution containing excess NaBr . Describe how the dyes ionize.

7. Speculate as to what salts would be predominantly surface-adsorbed by the precipitate in contact with a supernate containing the designated solutes at equimolar concentrations. (a) SrSO_4 in a supernate containing NO_3^- , Cl^- , and Ac^- as Sr^{2+} salts. (b) PbCrO_4 in a supernate containing Cl^- and NO_3^- as Pb^{2+} salts. (c) $\text{Al}(\text{OH})_3$ in a supernate containing Ba^{2+} , Sr^{2+} , Ca^{2+} , K^+ , and Na^+ as chlorides. (d) $\text{Al}(\text{OH})_3$ in a supernate containing OH^- , CrO_4^{2-} , $\text{Fe}(\text{CN})_6^{3-}$, and NO_3^- as K^+ salts.

8. When AgCl is formed by adding AgNO_3 solution to NaCl solution, the colloidal AgCl first formed coagulates very readily in the region where the AgNO_3 is about equivalent to the NaCl . Explain. (Consider the charge on the particles as the system passes through the equivalence point.)

9. Colloidal CaF_2 is suspended in a dilute solution containing about equimolar concentrations of $\text{Ba}(\text{NO}_3)_2$, MgCl_2 , and NaCl . What are the adsorbed and counter ions? Explain what electrolyte might be used to cause coagulation. Name an electrolyte in which CaF_2 could be suspended to produce a charge opposite to that above, and name the adsorbed and counter ions.

10. Describe an experimental method by which the sign of the charge on a colloid may be determined.

11. Pure, finely divided AgI is put into pure water, and negatively charged colloidal particles are formed. How do these particles obtain their charge (K11)? What does this imply as to the strict equivalence of Ag^+ and I^- in solution?

Section 12D

1. State whether the errors are probably positive or negative in the coprecipitation of (a) Li_2SO_4 with SrSO_4 in the determination of Sr; (b) $\text{Sr}(\text{NO}_3)_2$ with SrSO_4 in the determination of Sr; (c) BaCl_2 with BaSO_4 in the determination of Ba; (d) Ag_2SO_4 with BaSO_4 in the determination of sulfate; (e) $\text{Fe}_2(\text{SO}_4)_3$ with $\text{Fe}(\text{OH})_3$ in the determination of Fe; (f) $\text{Mg}(\text{OH})_2$ with $\text{Fe}(\text{OH})_3$ in the determination of Fe; (g) $\text{Na}_2\text{C}_2\text{O}_4$ with CaC_2O_4 in the determination of oxalate if the oxalates are ignited to carbonates at 485°C ; (h) $(\text{NH}_4)_2\text{C}_2\text{O}_4$ with CaC_2O_4 in the determination of oxalate, if the precipitate is ignited to CaCO_3 at 485°C .

2. Why should a strained region of a crystal have a higher solubility than an unstrained region?

3. How might it be possible to decide experimentally whether a particular contamination occurs predominantly by (a) surface adsorption, (b) isomorphic carrying, or (c) occlusion?

4. A precipitate is found to coprecipitate about the same amount of impurity, whether the precipitate is formed in the presence of the impurity, or whether the impurity is not added until after the precipitate is already formed. The extent of coprecipitation is small, only a few tenths of a per cent of the total coprecipitable impurity being carried. What is probably the predominant mechanism of contamination? How might this contamination be reduced?

5. A metal-salt impurity is present to the extent of about 1% in another sought-for metal salt. When the sought-for metal is precipitated, almost all the impurity is carried. Extensive washing does not remove the impurity. What might be the mechanisms of contamination? Describe further work that might permit differentiation among the suggested mechanisms.

6. An unsatisfactory, impure precipitate is analyzed and found to contain about the same type and proportion of impurities as are in the mother liquor. What is probably the mechanism of contamination, and how might it be reduced?

7. Suppose that there is present in solution an impurity that forms a double compound with a sought-for substance when the substance is precipitated. Suppose, however, that the concentration of impurity is kept low, and conditions of precipitation are maintained so that the solubility of the double compound is not exceeded. Why might the impurity still be expected to contaminate the sought-for precipitate?

8. Outline a process for preparing very pure BaSO_4 .

9. The carrying of traces of Pb^{2+} as PbSO_4 by BaSO_4 is classified as isomorphic coprecipitation. Classify the type of contamination when the BaSO_4 host is formed in a solution with Pb^{2+} sufficiently high so that the solubility product of PbSO_4 is exceeded, and tell how the precipitate may differ in nature from that containing only traces of Pb^{2+} .

10. An unknown solution of $\text{Fe}(\text{NO}_3)_3$ is titrated with standard NaOH to a phenolphthalein end point. How would the calculated amount of Fe differ from the true amount?

11. A 50-ml aliquot of a solution contains about 0.1 M each of ZnCl_2 , FeCl_3 , NaCl , and HCl . It is analyzed gravimetrically for the Fe content by adding water, heating, and adding dilute NH_3 to precipitate $\text{Fe}(\text{OH})_3$. The precipitate is digested, filtered, washed, ignited, and weighed. With good and careful techniques, the Fe content is invariably several per cent above the true value. Speculate on the nature of the error, and tell what might be done to decrease it.

12. $\text{Fe}(\text{OH})_3$ is so insoluble that Fe^{3+} may be thrown down quantitatively in rather acid solutions (pH 3). In separating Fe^{3+} from Ba^{2+} , would it be better to precipitate in an acid or a basic medium?

13. A solution contains barium and a small amount of lead, as the chlorides. The barium is precipitated in the presence of lead by adding an excess of sulfate, and part of the lead is isomorphically coprecipitated. Lead sulfate is soluble in ammonium acetate. Explain why all the lead cannot be extracted from the precipitate by digestion with ammonium acetate. Outline how you would determine the barium content of the original solution to reduce this error, giving reasons for the steps in your procedure.

PROBLEMS

Section 12C

1. Calculate the specific surface of a solid of density 3.00 g/cc, which is in the form of cubes 0.100μ on an edge. *Ans.* $2.0 \times 10^5 \text{ cm}^2/\text{g}$.

2. (a) What is the specific surface of 1.00 g of material (density = 1.00 g/cc) in the form of a single, spherical particle? (b) What is the specific surface of 1.00 g of this material divided into small, spherical particles, each of diameter d ? (c) What is the specific surface of 1.00 g of this material divided into small spherical particles of diameter 0.0100μ ? Compare answers with those for cubic particles (p. 188).

Section 12D

1. 1.000 g of Fe is precipitated as hydrated Fe_2O_3 . During ignition to dryness, 90% of the Fe is converted to Fe_2O_3 , but the remainder is improperly converted to Fe_3O_4 . What does the improperly ignited precipitate weigh? What should it weigh, were all the Fe in the proper form of Fe_2O_3 ? What is the percentage error of the analysis? *Ans.* 1.425 g; 1.430 g; -0.3%.

2. If 1.0% of the SO_4^{2-} were converted to Na_2SO_4 instead of quantitatively to BaSO_4 in a gravimetric sulfate analysis, what would be the error?

3. What is the percentage loss of Ba in Ex. 2, page 196? *Ans.* 2.0%.

4. Make the incorrect assumption referred to in Ex. 2, page 196, and show that the answer obtained is inconsistent with this assumption.

5. A solution contains 0.01000 M $\text{Zn}(\text{NO}_3)_2$ and 0.001000 M AgNO_3 . A 150.0-ml portion is treated with 151.0 ml of 0.01000 M Na_2CO_3 to precipitate ZnCO_3 in order that it may be recovered. Calculate the composition of the final solution and precipitate. What per cent of the Zn remains unprecipitated? *Ans.* $[\text{Zn}^{2+}] =$

$6 \times 10^{-7} M$; $[\text{Ag}^+] = 4.80 \times 10^{-4} M$; $[\text{CO}_3^{2-}] = 2.4 \times 10^{-5} M$; $[\text{NO}_3^-] = 0.01048 M$; $[\text{Na}^+] = 0.01004 M$; 0.0036 mole Ag per mole of Zn in ppt; 0.012% unprecipitated.

6. A solution contains 0.01000 M $\text{Pb}(\text{NO}_3)_2$ and 0.01000 M $\text{Ba}(\text{NO}_3)_2$. A 100.0-ml portion is treated with 100.0 ml of 0.02010 M NaIO_3 to precipitate $\text{Pb}(\text{IO}_3)_2$ so that it may be recovered. Calculate the composition of the final solution and precipitate. What per cent of the Pb^{2+} remains unprecipitated?

7. The Cu-group sulfides are insoluble in a solution containing 0.1 M HCl and saturated with H_2S . The Zn-group sulfides are said to be "soluble" in such a solution, and the two groups are separated on this basis. In 0.1 M HCl saturated with H_2S , $[\text{S}^{2-}]$ may be calculated to be about $10^{-20} M$. Such a solution is buffered with respect to S^{2-} , which means that $[\text{S}^{2-}]$ remains quite constant, even though appreciable amounts of S^{2-} may be removed from the solution to precipitate insoluble metal sulfides. From the solubility-product values in Appendix V, calculate the solubilities of the various forms of ZnS in this solution. Speculate on the conditions under which the sphalerite type of precipitate might form and cause the separation to fail.

Ans. $8.8 \times 10^{-5} M$ (sphalerite); 0.020 M (wurtzite); 0.11 M (pptd.).

13 GRAVIMETRIC METHODS

13A. COMMON GRAVIMETRIC METHODS

Table 13.1 summarizes some gravimetric methods of analysis for common elements. These methods are recommended by the American Society for Testing and Materials (A12) or the Association of Official Agricultural Chemists (A14). Obviously, special conditions, accuracy, interferences, separations, and applications cannot be given here, for they are beyond the scope of a tabular summary. For any one element there may be many separation and weighing forms besides those listed in Table 13.1. Choice of the most appropriate method for a particular purpose is governed by the amount and concentration of sought-for substance, interferences, accuracy desired, and the other factors described in Chapter 2. Details on gravimetric methods may be found in the literature (see Chapter 24). A new and most outstanding treatise on methods of analysis for the elements is that by Kolthoff and Elving (K13). Good data on the drying and ignition of many precipitates are given by Duval (D13).

13B. GRAVIMETRIC ERRORS

The following outline is a summary of the more frequently encountered sources of error, classified according to the sequence of operations as generally performed in a gravimetric analysis (Chapter 2). Most of these errors are discussed in other parts of the text, to which reference may be made. The outline may be useful as a check list, to avoid

sources of error in planning a determination, or in searching for sources of error.

- I. Inadequate method
 - A. Inadequate for amounts or concentrations of sought-for substance present
 - B. Inadequate provision for interferences
 - C. Inadequate accuracy
- II. Sample preparation
 - A. Contaminated sample
 - B. Nonrepresentative sample
 - C. Sample change due to improper storage
- III. Weighing sample
 - A. Incomplete drying (container and/or sample)
 - B. Inaccurate or nonreproducible weighing methods
- IV. Incomplete solution of sought-for substance
- V. Incomplete separation from interferences
 - A. Sought-for substance lost during removal of interfering substances
 - B. Incomplete removal of interferences
- VI. Precipitation, filtering, and washing
 - A. Incomplete precipitation of sought-for substance
 1. Solubility of the precipitate
 2. Insufficient precipitant
 3. Insufficient time for complete precipitation
 4. Presence of substances that increase precipitate solubility
 - a. Inert electrolytes
 - b. Complexing interferences
 - c. Too large an excess of precipitant
 - d. Improper pH
 - B. Precipitate contamination
 1. By true precipitation
 2. By coprecipitation
 - C. Filtration
 1. Loss of sought-for precipitate by passage through filter
 - a. Precipitate improperly formed or too fine
 - b. Filter too coarse
 2. Loss of filter material
 - a. Solubility in mother liquor or wash liquid
 - b. Mechanical loss, as in disruption of a Gooch mat and loss of fibers
 - D. Washing
 1. Solubility in wash liquid
 2. Reaction with wash liquid
 3. Peptization
 4. Insufficient washing
- VII. Ignition or drying of the precipitate
 - A. Insufficient ignition
 1. Failure to achieve proper form of precipitate
 2. Failure to burn off filter paper
 - B. Overignition
 1. Decomposition of precipitate
 2. Loss in weight of container

TABLE 13.1. GRAVIMETRIC METHODS FOR SOME COMMON ELEMENTS*

Element	Precipitant	Precipitated Form	Wash	Weighing Form	Ignition Temp. (°C)	Remarks
Aluminum.....	NH ₃ ; NH ₄ Cl (NH ₄) ₂ HPO ₄ ; NH ₃ 8-hydroxyquinoline; NH ₃	Al(OH) ₃ AlPO ₄ Al oxinate	NH ₄ Cl NH ₄ NO ₃ H ₂ O	Al ₂ O ₃ AlPO ₄ Al(C ₂ H ₃ ON) ₃	1200 1000 130	Precede by Al(OH) ₃ precipitation. Oxine ignitable to Al ₂ O ₃ at 1200°.
Antimony†.....	H ₂ S; HCl	Sb ₂ S ₃	H ₂ S; HCl	Sb ₂ O ₃	600	Treat sulfide with HNO ₃ and ignite.
Barium.....	(NH ₄) ₂ Cr ₂ O ₇ ; HAc; NH ₄ Ac	BaCrO ₄	NH ₄ Ac	BaCrO ₄	110	Separate from Sr.
Beryllium.....	NH ₃ ; NH ₄ Cl	Be(OH) ₂	NH ₄ Cl	BeO	1200	
Bismuth.....	HCl H ₂ S; H ₂ SO ₄	BiOCl Bi ₂ S ₃	H ₂ O H ₂ S; HCl	BiOCl Bi ₂ O ₃	110 700	Dissolve sulfide, precipitate hydroxide, and ignite.
Cadmium.....	KCN; NaOH H ₂ S; H ₂ SO ₄	Cd CdS	Alcohol H ₂ O	Cd CdS	110 110	Electrolysis. CdS convertible to CdSO ₄ by H ₂ SO ₄ fuming.
Calcium.....	(NH ₄) ₂ HPO ₄ ; NH ₃ (NH ₄) ₂ C ₂ O ₄ ; NH ₃	Ca ₃ (PO ₄) ₂ CaC ₂ O ₄	NH ₄ NO ₃ H ₂ O	CaSO ₄ CaO CaSO ₄	1000 950 1000	Treat phosphate with H ₂ SO ₄ . Ignite oxalate. Ignite oxalate with (NH ₄) ₂ SO ₄ .
Carbon (CO ₂)....				CO ₂		Weight loss on ignition, or weight gain of absorbent for CO ₂ . Organic compounds, steels, carbonates.
Chlorine.....	AgNO ₃ ; HNO ₃	AgCl	NH ₄ NO ₃	AgCl	150	
Cobalt†.....	α-nitroso-β-naphthol; HCl	Co α-nitroso-β-naphtholate	HCl	Co ₂ O ₃ Co	850	CoO formed above 900°C. Ignite oxide in H ₂ .
Copper.....	HNO ₃ ; H ₂ SO ₄ H ₂ S; H ₂ SO ₄	Cu CuS	Alcohol H ₂ S; H ₂ SO ₄	Cu CuO	110 1000	Electrolysis. Ignite sulfide in air.
Hydrogen.....				H ₂ O		Weight loss on ignition, or weight gain of absorbent for H ₂ O. Organic compounds, hydrates.
Iodine†.....	AgNO ₃ ; HNO ₃	AgI	HNO ₃	AgI	110	Electrolysis (on anode).
Lead.....	HNO ₃ K ₂ Cr ₂ O ₇ ; NH ₄ Ac; HAc H ₂ SO ₄ ; HNO ₃ (NH ₄) ₂ MoO ₄ ; NH ₃	PbO ₂ PbCrO ₄ PbSO ₄ PbMoO ₄	H ₂ O H ₂ O H ₂ O NH ₄ NO ₃ ; NH ₃	PbO ₂ PbCrO ₄ PbSO ₄ PbMoO ₄	120 105 600 650	
Lithium.....	Conc. HCl	LiCl	Alcohol; ether	Li ₂ SO ₄	700	Alcohol-ether wash extracts and separates LiCl from NaCl and KCl. Fume LiCl with H ₂ SO ₄ .
Magnesium.....	(NH ₄) ₂ HPO ₄ ; NH ₃	MgNH ₄ PO ₄ ·6H ₂ O	NH ₄ NO ₃ ; NH ₃	Mg ₂ P ₂ O ₇	1050	

Mercury.....	H ₂ S; H ₂ SO ₄	HgS	H ₂ O	HgS	110	Volatility of Hg utilized in separations.
Molybdenum.....	α-benzoin oxime; H ₂ SO ₄ H ₂ S; H ₂ SO ₄	Mo salt of oxime MoS ₃	Oxime H ₂ SO ₄ H ₂ S; H ₂ SO ₄	MoO ₃ MoO ₃	525 525	Volatilizes above 600°C. Ignite sulfide to oxide.
Nickel.....	NH ₃ Dimethylglyoxime; NH ₃	Ni Ni(C ₄ H ₇ O ₂ N ₂) ₂	Alcohol Oxime; NH ₃	Ni Ni(C ₄ H ₇ O ₂ N ₂) ₂	110 150	Electrolysis. Very selective.
Niobium.....	HClO ₄	Nb ₂ O ₅ (hydrous)	HCl	Nb ₂ O ₅	1050	
Phosphorus.....	MgSO ₄ ; (NH ₄) ₂ SO ₄ ; NH ₃	MgNH ₄ PO ₄ ·6H ₂ O	NH ₄ NO ₃ ; NH ₃	Mg ₂ P ₂ O ₇	1050	Precede by separation as (NH ₄) ₃ PO ₄ · 12MoO ₃ .
Potassium.....	Conc. HCl	KCl	Evaporate to dryness	KCl	600	
				KClO ₄	350	Fume KCl with HClO ₄ .
				K ₂ NaCo(NO ₂) ₆	100	Separation from Na.
				K ₂ PtCl ₆	100	
Selenium.....	NH ₂ CO(NO ₂) ₂ ; HNO ₃ H ₂ PtCl ₆ ; alcohol	Se	H ₂ O	Se	85	
Silicon.....	NH ₂ OH·HCl	SiO ₂ (hydrous)	HCl	SiO ₂	1100	Volatilize SiO ₂ with HF, and measure weight loss.
Silver.....	HClO ₄ KI; HNO ₃ HCl; HNO ₃	AgI AgCl	HNO ₃ HNO ₃	AgI AgCl Ag	110 400	
Sodium.....	Conc. HCl	NaCl	Evaporate to dryness	NaCl	600	Dry reduction of AgCl with Pb.
				NaMg uranyl ace- tate	350	Volatilizes above 850°C. Fume NaCl with HClO ₄ . Soluble in organic solvents, allowing separation from K.
				NaMg uranyl ace- tate	110	May also, precipitate NaZn uranyl acetate as weighing form.
Strontium.....	UO ₂ Ac ₂ ; MgAc ₂ ; HAc	SrSO ₄	Reagent; alcohol	NaMg(VO ₂) ₂ (C ₂ H ₅ O) ₉ ·6H ₂ O	800	
Sulfur.....	H ₂ SO ₄ ; alcohol	BaSO ₄	Alcohol-ether	SrSO ₄	1050	For sulfate only.
Tantalum.....	BaCl ₂ ; HCl	Ta ₂ O ₅ (hydrous)	H ₂ O	BaSO ₄	105	
Thallium.....	HClO ₄	TlI	HCl	Ta ₂ O ₅	1100 1100	Ignite sulfide to oxide.
Tin.....	H ₂ SO ₄ ; NaHSO ₄ ; KI	SnO ₂ (hydrous) SnS	KI; alcohol	TlI	750	Volatilizes above 750°C.
Tungsten.....	HNO ₃ H ₂ S; H ₂ SO ₄	WO ₃ (hydrous)	H ₂ O NH ₄ Ac; HAc	SnO ₂ SnO ₂	950 105	Ignite ZnS to ZnO. Precede with ZnS precipitation.
Zinc.....	H ₂ SO ₄ (NH ₄) ₂ Hg(SCN) ₄ ; H ₂ SO ₄ 8-hydroxyquinoline; HAc; NH ₄ Ac	ZnS ZnHg(SCN) ₄	HCl	WO ₃	140	
Zirconium.....	(NH ₄) ₂ HPO ₄ ; H ₂ SO ₄	Zn(C ₂ H ₅ ON) ₂ Zr(HPO ₄) ₂	H ₂ O NH ₄ NO ₃	ZnO ZnHg(SCN) ₄ Zn(C ₂ H ₅ ON) ₂ ZrP ₂ O ₇	1050	

* Elements omitted from this table are the less common ones, or, if common, they are rarely determined gravimetrically.

† Rarely determined gravimetrically.

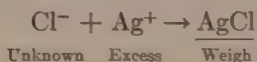
- C. Reaction between precipitate and filter medium
 - 1. Reduction of precipitate by filter paper
 - 2. Fusion of precipitate with porcelain glaze
 - 3. Alloying or reduction of precipitate with metal crucible
 - D. Absorption of H_2O or CO_2 from atmosphere or desiccant
- VIII. Computational errors, including improper corrections

13C. GRAVIMETRIC EXPERIMENTS

Two gravimetric determinations suitable for student performance are described in considerable detail—the determination of chloride as $AgCl$, and of sulfate as $BaSO_4$. The notes given with these experiments typify the detailed knowledge and comprehension needed to perform any chemical analysis accurately and efficiently. The analyst may work his way through the procedure without studying this detail beforehand, but in so doing he becomes vulnerable to a host of errors and inefficiencies that decrease his chances of good work. Any other analysis that is performed by the student is worth a similarly detailed study.

EXPERIMENT 13.1. GRAVIMETRIC DETERMINATION OF CHLORIDE AS $AgCl$ *

The chloride in a water-soluble sample containing only $NaCl$ and KCl is precipitated as $AgCl$ with an excess of $AgNO_3$. The Cl content of the original sample is calculated from the weight of $AgCl$ obtained.



This method is sufficiently accurate for atomic-weight determinations (C2, S8). Chloride analysis is frequently encountered, for chloride is widely distributed in both manufactured and natural materials. Extensions and applications of this method are described in the Supplement (p. 733).

PROCEDURE

For techniques, read the introduction to Chapter 8 (p. 96).

1. Mark and clean three filtering crucibles, and heat for 1–2 hours in the 150 – $160^\circ C$ oven. Cool for one hour in the desiccator and weigh each crucible. Repeat the washings and heatings until constant weight is attained within 0.2 mg. (Note 1.)

* A 45-minute film on gravimetric techniques, built around the determination of chloride, is available from the Television Laboratory, University of Wisconsin, Madison, Wisconsin. There is also a supplementary 20-minute reel on filtration with paper and with the Gooch crucible.

2. Dry the sample 2 hours in a small weighing bottle in the 105–110°C oven.

3. Weigh indirectly to the nearest 0.1 mg three samples of 0.26–0.41 g each into clean, dry, unscratched, and properly marked 250-ml beakers. (Note 2.)

4. After testing reagents (Note 3), take each sample up in about 100 ml of water containing 1–2 ml of conc. HNO_3 . (Note 4.)

5. Calculate how much 0.5 M AgNO_3 reagent is required theoretically to precipitate the chloride in each sample, and then use 10% in excess of this. (Notes 5, 6.) Dilute the concentrated shelf reagent about five-fold before addition, and add the diluted solution dropwise from a 50-ml pipet to the sample solution at room temperature, stirring during the addition. (Notes 7, 8.)

6. After the AgNO_3 is added, heat the solution almost to boiling for about 15 minutes, stirring occasionally. (Note 8.) Cover and set away in locker to digest overnight. (Notes 9–12.)

7. After the supernate is clear, test it for complete precipitation before filtration by adding a drop of 0.5 M AgNO_3 . (Note 13.)

8. Decant the clear supernate at room temperature (Note 14) through the previously weighed filter crucible. (Note 15.)

9. Wash the bulk of precipitate in the beaker twice by decantation with about 25-ml portions of 0.01 M HNO_3 . (See Appendix IVB for concentrations of common reagent solutions.) Then transfer the bulk of precipitate quantitatively to the filter and wash three times with 0.01 M HNO_3 from a small wash bottle. (Notes 16, 17.) Test the last wash portion for completeness of washing by adding a drop of 1 M HCl . Continue washing if more turbidity forms than is given by an unused portion of the HNO_3 wash solution.

10. Remove the crucible, wipe excess water and lint from the outside with a clean towel, and dry in the 150–160°C oven for 2 hours. (Note 18.) Cool in the desiccator and weigh. Repeat the drying, cooling, and weighing until constant weight is obtained within 0.2 mg. (Note 19.)

11. From the weight of AgCl obtained, calculate the % Cl in the sample for each determination. (Note 20.) Calculate the average % Cl , and the range. (Note 21.) Report results according to the form requested by the instructor. (Note 22.) The summary data page shown on page 216 is typical.

NOTES

(1) Sintered glass crucibles are easiest to use and give the best accuracy. Gooch crucibles or glass-fiber filter disks in perforated crucibles are also satisfactory. Filter paper is undesirable because AgCl is reduced and decomposed to Ag and Ag_2O upon

SUMMARY DATA PAGE

EXP. 13.1. GRAVIMETRIC CHLORIDE

Date begun.....

John Brown

Date completed.....

Locker No....

Determination	I	II	III
Identifying marks on crucible			
Wt. crucible, 1 heating (data, p.)			
2 heatings			
3 heatings			
Sample wt. (data, p.)			
Wt. bottle with sample			
Wt. bottle less sample			
Wt. sample			
Wt. crucible plus AgCl (data, p.)			
1 heating			
2 heatings			
3 heatings			
Wt. AgCl			
% Cl in sample (calcs., p.)			
Average % Cl			
Range, % Cl			
Range, relative, %			

ashing. Reconversion to AgCl is troublesome. Also, AgCl is appreciably volatile at ashing temperatures.

In taking the crucible to constant weight, it should not only be heated between weighings, but about 100 ml of water containing 1-2 ml conc. HNO_3 should also be passed through the mat.

(2) A weight of sample should be used that is sufficient to give 0.5-1.0 g AgCl. For the pure NaCl-KCl samples used in this determination, the sample size is selected as follows:

The weight of pure KCl required to give 0.50 g AgCl is $(0.50/143.32)(74.56) = 0.26$ g. If this weight of NaCl were taken, the weight of AgCl produced would be $(0.26/58.44)(143.32) = 0.64$ g, somewhat more than the desired lower limit (0.50 g) of AgCl. The lower limit of sample size is therefore 0.26 g.

The weight of pure NaCl required to give 1.00 g AgCl is $(1.00/143.32)(58.44) = 0.41$ g. If this weight of pure KCl were taken, the weight of AgCl produced would be somewhat less than the desired upper limit (1.00 g) of AgCl. The upper limit of sample size is therefore 0.41 g.

If the approximate Cl content is not deducible from the sample history, it is necessary to guess at the sample size. If the amount chosen does not give an appropriate weight of precipitate, a second sample size must be chosen in the light of results on the first. Generally, the instructor will announce the proper sample size. Unknown sample preparation is discussed in the Supplement (p. 741).

(3) Chloride is an almost universal contaminant, and its absence from the reagents must be assured before the analysis is begun. Only a negligible turbidity should be produced when a few drops of 0.5 *M* AgNO₃ are added to 100 ml of water containing 1–2 ml of conc. HNO₃. Reject the test portion.

(4) Many anions form Ag salts that are insoluble in neutral solution but soluble in acid. Among these are the anions of weak acids, such as OH[−], CN[−], BO₂[−], CO₃[−], C₂O₄[−], PO₄[−], AsO₄[−]. An HNO₃ concentration of 0.1–0.3 *M* is sufficient to prevent simultaneous precipitation of these anions as the Ag salts. The following equilibria describe the behavior of CO₃[−], which may enter the solution from air.



However, even in acid solution there is still a tendency for these anions to coprecipitate, and they may cause error if present in significant amounts. A more complete account of interferences is given on page 220.

(5) The approximate composition of the sample again must be known for this computation. Since a pure NaCl sample would have the maximum Cl content, the maximum volume of 0.50 *M* AgNO₃ required for precipitation of *S* g of sample would be

$$\frac{S}{58.44} \times 1.10 \times \frac{1}{0.50} \times 1000 = 38S \text{ ml}$$

$\underbrace{\hspace{10em}}_{\text{moles NaCl in } S \text{ g of sample} = \text{moles AgNO}_3 \text{ required}}$
 $\underbrace{\hspace{10em}}_{\text{moles AgNO}_3 \text{ required plus 10\% excess}}$
 $\underbrace{\hspace{10em}}_{\text{liters of 0.50 } M \text{ solution required}}$

(6) Any encrustation at the lip of the reagent bottle should be removed before pouring, wiping with a piece of damp tissue, if necessary. After pouring, blot off any solution adhering to the lip with a clean tissue. Use the expensive 0.5 *M* AgNO₃ solution very sparingly, withdrawing only what is needed. Any excess that is inadvertently withdrawn should not be returned to the reagent bottle, but should be put into the "Silver Residues" storage bottle.

(7) These measures are used to reduce contamination of the precipitate. For the same reason, a very large excess of AgNO₃ should not be used. A moderate excess (a few hundredths molar) will not cause serious error.

(8) From the standpoint of reducing coprecipitation, it would probably be well to carry out the precipitation in hot solution. However, as long as there is appreciable unprecipitated chloride, heating causes loss through oxidation by the nitrate.



(Volatile NOCl is also formed.) Even that part of the chlorine that is not lost from solution is not quantitatively precipitated by excess AgNO₃, since



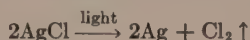
AgOCl is soluble in acid solution, and its chlorine content remains unprecipitated. After excess AgNO₃ is added, however, the solution may be heated, for then the chloride concentration is so low that the rate of oxidation is inappreciable even in hot solution.

(9) For storage, the beaker should be well covered, preferably placed inside an inverted beaker of larger size, so that HCl fumes may not gain entrance to the solution. This is especially necessary if concentrated acid reagent bottles are kept in the locker. The cover is also useful to keep out dust, which may be organic in nature and may later cause decomposition of the AgCl on drying.

(10) If the precipitation is made near the beginning of the working period, the supernate should be inspected after a half hour. If the supernate is quite clear, it is advisable to make the test for complete precipitation at this time, rather than immediately before filtration. Considerable time may be saved if incomplete precipitation is discovered early, rather than just before filtration.

(11) The time of digestion is not critical. The minimum time is that required for the precipitate to settle sufficiently to give a fairly clear supernate, so that a test for complete precipitation may be made. Longer digestion is not harmful, and it may be convenient to let the precipitate digest until the next working period.

(12) Once formed, the precipitate should be kept away from daylight or bright artificial light because of photodecomposition. Since the digestion may extend over several days, the (dark) locker is chosen for storage.



The sign of the error will depend on the point in the analysis at which decomposition occurs. If decomposition occurs while the AgCl is still in contact with the mother liquor, the result is high. The chlorine liberated reacts with water to form more Cl⁻ (Note 8), which in turn precipitates more of the excess Ag⁺. In a typical analysis, 5 hours in direct sunlight gave results about 2% high, whereas 2 hours in a brightly lighted laboratory gave results only about 0.2% high.

On the other hand, if the decomposition occurs after separation of the AgCl from the mother liquor, chlorine escapes and the result is low. Reduction is faster for a moist precipitate than for a dry one. Thus for dry AgCl, losses of only 0.01–0.1% were observed for 2–7 hours of exposure in a brightly lighted laboratory, with no direct or reflected sunlight (L17). The metallic Ag that is produced imparts a purplish, gray, or black coloration to the AgCl. Reduction occurs only on the surface of the AgCl, and considerable blackening may occur without appreciable change in weight.

(13) If a precipitate forms, it is necessary to add more AgNO₃, and to heat and digest again as directed in steps 5 and 6.

(14) The solubility of AgCl increases very rapidly with temperature, so that hot filtration and washing cannot be used.

*HOCl is itself light-sensitive and is slowly decomposed to a variety of products, among which are HCl, O₂, and HClO₂. This does not invalidate the foregoing argument, for even if the HClO is decomposed, some of the chlorine remains in a form (chlorate) that is not precipitable by silver ion (A4).

(15) Examine especially the first portions of filtrate for turbidity, and for asbestos needles if a Gooch crucible is used. Repass through the filter if necessary.

(16) AgCl is a hydrophobic colloid that is coagulated in the mother liquor principally by the HNO_3 and excess AgNO_3 . If these adsorbed electrolytes are removed by washing with pure water, peptization and loss of precipitate occur. By using dilute HNO_3 in the wash liquid, sufficient electrolyte will always be present to prevent peptization. HNO_3 replaces the adsorbed nonvolatile electrolytes (Ag, K, and Na nitrates). A small amount of HNO_3 retained by the precipitate causes no error, since it is volatilized on drying.

(17) Since AgCl is not extremely insoluble, washing should be done sparingly.

(18) If there is time, it is well to air-dry the precipitate first, either overnight in a covered vessel or in the $105\text{--}110^\circ\text{C}$ oven. If the precipitate is dried very rapidly, it apparently shrinks and traps water in the interstices, and greater difficulty may be experienced in drying to constant weight. AgCl seems to hold tenaciously to the last traces of water. A few hundredths of a per cent of water is retained even after drying to constant weight at $110\text{--}120^\circ\text{C}$, and 0.01% is retained at 280°C . To remove the last traces of water, the AgCl must be heated to the melting point (460°C). This procedure is not recommended because of the volatility of AgCl at high temperatures, and because of the increased chances of decomposition. Another procedure is to dry in air or in a vacuum desiccator at room temperature after passing acetone or alcohol through the precipitate on the filter. Drying by this method seems less complete than by heating, although some authors claim that the method is as efficient as drying by melting.

(19) The dried AgCl is not hygroscopic, and the weighing may be performed in an uncovered crucible without appreciable uptake of moisture by the precipitate during weighing. However, cooling and storage should still be done in the desiccator, especially if a Gooch crucible is used.

(20) If W g of the AgCl are obtained from S g of sample, the % Cl in the sample is

$$\frac{W}{143.32} \times 35.453 \times \frac{100}{S} = \% \text{ Cl in sample}$$

\downarrow g Cl in sample
 \downarrow moles AgCl = moles Cl in sample

This equation should be perfectly understood and derivable by the student. Under no circumstances should it be memorized or used uncritically, for it is easier to go through the reasoning than to memorize it. In fact, it is suggested that the student use whatever method of calculation he understands best. The equation above is intended as a guide to students who have difficulty with the calculations, and not as a means to avoid the fundamental reasoning. In most future experiments the student is left to devise his own method of calculation, without equations such as this to guide him.

(21) For excellent work, the relative range of triplicates is about 0.2% , and the relative error of the average is less than 0.1% . Relative errors of only a few thousandths of a per cent are achievable. The extreme precautions necessary at this error level have been interestingly summarized (C2, S8).

(22) Save crucibles and precipitates in the desiccator until grades are returned. Then put AgCl in "Silver Residues" bottle. To clean the crucibles, most particles may be removed by gentle rubbing under a stream of water. Embedded particles

may be picked out with a needle or dissolved by successive treatments with conc. HNO_3 , water, and conc. NH_3 .

CHEMICAL INTERFERENCES

Because most chlorides are soluble, the specificity of the AgCl procedure is good. The accuracy is high and not critically dependent on conditions. It is rather remarkable, also, that coprecipitation is so low. Apparently the spongy nature of the precipitate allows it to come easily into equilibrium with the solution in which the precipitate is immersed, and adsorbed impurities are easily removed by washing. Chemical interferences, however, are of several kinds.

1. Anions that form Ag salts that are insoluble even in acid solution are: SCN^- , Br^- , I^- , CN^- , $\text{S}^{=}$, $\text{S}_2\text{O}_3^{=}$, $\text{Fe}(\text{CN})_6^{=}$, and $\text{Fe}(\text{CN})_6^{4-}$. These precipitate simultaneously with AgCl , causing positive error. Before the AgCl is precipitated these anions must be destroyed or removed from solution. Anions forming Ag salts soluble in acid were discussed in Note 4 above.

2. Cations may interfere in the following ways: (a) If Ag^+ , Hg_2^{2+} , or moderate amounts of Pb^{2+} are present in the sample, they exist as insoluble chlorides. The chloride must be liberated from these cations before it may be precipitated as AgCl . Boiling with concentrated Na_2CO_3 solution may accomplish this separation, as described in the Supplement (p. 739). (b) Hg^{2+} , Cd^{2+} , Sn^{2+} , Sb^{3+} , Cr^{3+} , and Pt^{4+} form soluble complexes with chloride. They compete with Ag^+ , keeping the sought-for chloride in solution and making results low. (c) Sb^{3+} and Bi^{3+} hydrolyze even in moderately strong acid solution, forming SbOCl and BiOCl , which precipitate to give high results. Some of these metallic ion interferences may be removed by precipitation with NH_3 or K_2CO_3 , but care must be used to prevent coprecipitation and loss of chloride.

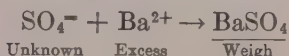
3. Even anions forming soluble Ag salts or cations forming soluble chlorides may coprecipitate with AgCl at high concentrations. Thus sulfate is tolerable at moderate concentrations, but causes positive error at higher concentrations, possibly due to coprecipitation of Ag_2SO_4 . Similar errors are caused by Pt and Pd .

4. Reducing agents may reduce Ag^+ to metallic Ag , causing positive error. Many organic substances, such as formaldehyde, act in this way. Sn^{2+} and SO_2 are examples of inorganic reducers. These interferences may be eliminated by oxidation. H_2O_2 is frequently used as an oxidizing agent, since excess H_2O_2 is easily destroyed by boiling.



EXPERIMENT 13.2. GRAVIMETRIC DETERMINATION OF SULFATE AS BaSO_4 *

The sulfate in a water-soluble sample containing only Na_2SO_4 and NaCl is determined by the precipitation and weighing of BaSO_4 .



This method is widely applicable to many kinds of S-bearing samples, as described in the Supplement (p. 737). Although capable of fairly good results, the method is liable to coprecipitation, and is considerably less accurate than the determination of chloride as AgCl .

PROCEDURE

For techniques, read the introduction to Chapter 8 (p. 96).

1. Mark and clean three 00 crucibles and covers, and heat for a half hour in the electric furnace at 700°C , or at full heat of the Bunsen burner. Cool one hour in the desiccator and weigh each crucible with cover. Repeat heatings until constant weight is attained within 0.2 mg. (Note 1.)

2. Dry the sample in a small weighing bottle for 2 hours in the $105\text{--}110^\circ\text{C}$ oven. Weigh indirectly to the nearest 0.1 mg three portions of 0.30–0.37 g each into clean, dry, unscratched, and properly marked 400-ml beakers. (Note 2.) To each sample add about 150 ml of water, 2 drops of 1 *M* HAc, and 0.5 ml of 0.5 *M* NaAc. (Notes 3, 4.)

3. Prepare the precipitant by adding 2 drops of 1 *M* HAc and 0.5 ml of 0.5 *M* NaAc to 150 ml of water in a 250-ml beaker. Then add that volume of 0.5 *M* BaCl_2 required to react with the sample, plus a 10% excess. (Notes 5, 6.)

4. Heat the unknown and precipitant solutions just to boiling, and then pour the precipitant smoothly and rapidly into the unknown solution. Stir continuously and vigorously for 2–3 minutes, without splashing. (Note 7.) Allow the precipitate to settle sufficiently so that a test for complete precipitation may be made before the filtration is begun. (Notes 8, 9.)

5. To filter, decant the supernatant liquid through ashless, fine filter paper. (Note 10.) Wash the precipitate by decantation in the beaker with a 25-ml portion of hot water. Then transfer the precipitate quantitatively to the filter and wash three times with hot water from the wash bottle. (Notes 11, 12.)

6. Remove the paper from the funnel and fold it to fit in the weighed

* See footnote on motion picture film, page 214.

crucible. (Note 13.) Carefully burn off the paper, with free access to air. After paper is carbonized or burned off, ignite the covered crucible for a half hour in the electric furnace at 700°C , or at full heat of the Bunsen burner. Cool for an hour in the desiccator and weigh. Repeat the ignition until constant weight is attained within 0.3 mg. (Notes 14–16.)

7. Compute the % SO_3 in the sample for each determination. Calculate the average % SO_3 and the range. (Note 17.) Report results as requested by instructor. (Note 18.)

NOTES

(1) These directions apply to filtration through ashless filter paper, which is later burned off in an ordinary crucible. This method is chosen to extend the experience of the student, since a filter crucible was used in Exp. 13.1. A sintered porcelain or Gooch crucible is actually more accurate than filter paper for this determination.

(2) Each portion should give 0.4–0.6 g BaSO_4 , and the size is calculated as in Note 2, page 216. The recommended sample size of 0.30–0.37 g is for $\text{NaCl-Na}_2\text{SO}_4$ samples containing 80–100% Na_2SO_4 . Sample preparation is discussed in the Supplement (p. 741). If different samples are used, the appropriate sample size should be designated.

(3) Before adding water, HAc, and NaAc to the sample, test these reagents for contamination by performing step 3.

(4) The HAc and NaAc adjust the pH to about 5, assuming that the original sample is neutral. This assumption may be made unless the instructor directs otherwise. If the sample is acidic or basic, it must be neutralized before HAc and NaAc are added.

Errors may occur if the acidity is too high or too low. If the acidity is too high, there is a tendency toward occlusion of H_2SO_4 and alkali bisulfates, especially within the first portions of BaSO_4 , which are formed in a mother liquor containing excess sulfate. These bisulfates are decomposed and H_2SO_4 is volatilized on ignition, making the results low.



In basic solutions, CO_2 from the air may contaminate the precipitate with BaCO_3 . A more complete account of errors and interferences is given in the following section.

(5) Since some samples may run as high as 100% Na_2SO_4 , the amount of precipitant must be calculated on this basis. For S g of sample, the volume of 0.50 M BaCl_2 required would be

$$\frac{S}{142.04} \left| \begin{array}{l} \times 1.10 \\ \times \frac{1}{0.50} \end{array} \right| \times 1000 = 15.5S \text{ ml}$$

— 10% excess

— moles Na_2SO_4 in sample = moles BaCl_2 required

— liters of 0.50 M solution required

(6) If no precipitate forms after 10 minutes, the reagents are uncontaminated.

(7) The precipitation is carried out in hot, dilute, and slightly acid solution to reduce contamination. If the barium and sulfate concentrations in the reagent solutions are less than 0.02 M , slow addition is not necessary. These conditions are recommended by Fischer and Rhinehammer (F4).

(8) To test for complete precipitation, allow the precipitate to settle for about a quarter of an hour, or until the supernate is clear. Without disturbing the precipitate, add one drop of 0.5 *M* BaCl₂, and look for further precipitation where the drop falls into the solution.

(9) Digestion is not necessary, and filtration may be begun as soon as the beaker is cool enough to handle. However, it is advisable not to filter until the test for complete precipitation is made on the supernate. If the test for completeness is deferred until after filtration has begun, and if precipitation is incomplete, the situation is difficult to remedy because the sample is distributed among several containers.

(10) Examine the first portions of filtrate for small particles of precipitate, re-filtering if any are found. Also, test the first portion of clear filtrate once more for complete precipitation.

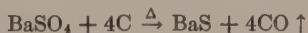
(11) Washing should be done sparingly, since BaSO₄ is only moderately insoluble; however, hot water may be used, since BaSO₄ is not much more soluble in hot water than in cold. Since there is no tendency toward peptization, an electrolyte need not be used in the wash water. There is a tendency toward loss of precipitate by "creeping" of the precipitate over the top edges of the filter paper. To reduce this, never fill the paper to the top, and keep washing on the filter to a minimum. When creeping is particularly troublesome, a wetting agent may be helpful (A7).

(12) Test the last wash portion for completeness of washing by adding one drop of 0.5 *M* AgNO₃, and continue washing if more turbidity forms than is formed by adding a drop of the AgNO₃ to an unused portion of wash water.

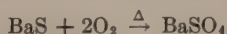
(13) If any precipitate has crept or spattered onto the upper edge of the funnel, wipe the edge with a small piece of damp, ashless filter paper, and add the piece to the crucible.

(14) BaSO₄ adsorbs water slowly, especially on humid days. All weighings should be made with a covered crucible.

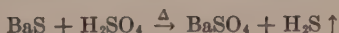
(15) While the filter paper is being burned off, the BaSO₄ may be partially reduced by carbon.



If this reaction occurs only slightly, the BaS is oxidized by continued ignition in the air after all carbon is burned off, and no error results.



If the reduction is extensive, as it may be if the temperature is raised too high before all carbon is burned off, the BaS formed may oxidize only slowly, and constant weight may not be achieved easily. In this case, add one drop of conc. H₂SO₄ to the residue, heat the covered crucible cautiously until the excess H₂SO₄ is completely driven off, and then reignite.



(16) Very high temperatures are required to dry the BaSO₄ completely. Precipitates dried at 105–110°C may contain several tenths of a per cent of water, which apparently forms a solid solution with the BaSO₄ (W4). Fortunately, BaSO₄ is stable, and high temperatures may be used to accelerate the drying process. Temperatures much in excess of 700°C should not be used, however, for the BaSO₄ will then react with the crucible glaze.

(17) For excellent work, the relative range of triplicates is around 0.3%, and the relative error of the average is around 0.2%.

(18) Save precipitates and remaining sample until grades are returned. For particles of BaSO_4 not removable from the crucible by gentle rubbing under a water tap, a hot 0.1 *M* solution of the disodium salt of ethylenediaminetetraacetic acid is a good solvent (B29).

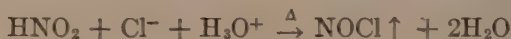
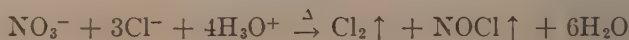
CHEMICAL INTERFERENCES

The principal source of error in the BaSO_4 procedure is coprecipitation. Practically all anions and cations are coprecipitated to some extent. Since there are no easy methods for dissolving BaSO_4 , reprecipitation cannot be used to reduce contamination; the only feasible methods are limited ones that must be applied before or during the precipitation process. The determination of BaSO_4 is more subject to interferences and more critically dependent on conditions than is the determination of AgCl , and the probable error is several times greater. Special methods of reducing these errors are described in the Supplement (p. 740). Chemical interferences may be classed as follows:

1. Although a number of anions form Ba salts that are insoluble in neutral solution, most of them are soluble in dilute acid. Among these anions are CO_3^{2-} , PO_4^{3-} , F^- , and CrO_4^{2-} . If precipitation of BaSO_4 is performed in dilute acid, moderate amounts of some of these anions are tolerable. (See Note 4, p. 217, for the action of acid in preventing interference by carbonate.) However, even in acid solution some of these anions show a marked tendency toward coprecipitation, even though the solubility products of the Ba salts may not be exceeded. Thus PO_4^{3-} and F^- interfere even at low concentrations in acid solution, and must be removed before precipitation. Also, CrO_4^{2-} is not tolerable in appreciable concentrations, since BaSO_4 and BaCrO_4 are isomorphic and form mixed crystals (W5).

2. If Ba^{2+} , Pb^{2+} , Sr^{2+} , or Ca^{2+} are present in the sulfate sample, the sulfate must be liberated and separated from these cations before it may be precipitated as BaSO_4 (see Supplement, p. 739).

3. Coprecipitation of various anions with BaSO_4 decreases in the order BrO_3^- , $\text{Fe}(\text{CN})_6^{4-}$, NO_3^- , ClO_3^- , MnO_4^- , $\text{Fe}(\text{CN})_6^{3-}$, ClO_4^- , Cl^- , Br^- , I^- , SCN^- , CH_3COO^- . Although moderate amounts of Cl^- do not cause serious error, NO_3^- , NO_2^- , ClO_3^- , and BrO_3^- must be removed before precipitation of BaSO_4 . This may be done by fuming the sample with conc. HCl .



Coprecipitation of cations decreases in the order Cd^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} , Al^{3+} , Fe^{2+} , K^+ , Ni^{2+} , Na^+ , Li^+ , Mg^{2+} . The cations Fe^{3+} and Cr^{3+} are more strongly coprecipitated than Cu^{2+} . In addition, Cr^{3+} forms soluble complexes with SO_4^{2-} to prevent complete precipitation. H^+ is coprecipitated quite strongly, but its exact position in the series is not known. K^+ is coprecipitated considerably more than Na^+ , since the ionic radius of K^+ is closer to that of Ba^{2+} . These alkali ions are apparently coprecipitated as the bisulfates, and the extent of contamination may be reduced by performing the precipitation at low acidity (pH 5–6) (F4). Some of these cation interferences may be removed by precipitation with Na_2CO_3 , NH_3 , or NaOH , care being used to prevent loss of sulfate by carrying. Other chemical methods of removing interferences may be used, as illustrated below for Fe^{3+} .

The interference of Fe^{3+} is particularly troublesome in many kinds of samples, but it may be removed in several ways. (1) By using NH_3 , $\text{Fe}(\text{OH})_3$ may be precipitated and removed before throwing down BaSO_4 . However, some sulfate tends to coprecipitate with the $\text{Fe}(\text{OH})_3$ as a basic salt. To prevent loss of this sulfate, the $\text{Fe}(\text{OH})_3$ is dissolved, reprecipitated, and the filtrate containing the recovered sulfate is added to the filtrate from the first precipitation, which contains the major fraction of the sulfate. (2) Fe^{3+} may be easily reduced to Fe^{2+} with a reducing agent such as hydroxylamine hydrochloride. Although Fe^{2+} is coprecipitated, it is tolerable in larger amounts for a given error than is Fe^{3+} . (3) Fe^{3+} may be complexed into a non-coprecipitable form. Tartrate or citrate accomplish this even in moderately acid solutions. Ethylenediaminetetraacetic acid is also an effective complexer (F4).

If the sought-for sulfate is precipitated by adding excess BaCl_2 slowly to Na_2SO_4 , the error is predominantly negative. If the Na_2SO_4 is added slowly to excess BaCl_2 , the error is predominantly positive, owing to coprecipitation of BaCl_2 . In a practical precipitation, both errors operate simultaneously. Thus even when BaCl_2 is added to excess Na_2SO_4 , there are high local concentrations of BaCl_2 in the regions where BaCl_2 falls into the Na_2SO_4 solution, and BaCl_2 may be occluded by crystals formed in this region. Thus both BaCl_2 and Na_2SO_4 are coprecipitated, the relative amounts of each being critically dependent upon conditions which are difficult to control.

QUESTIONS

Sections 13A, B

1. Criticize the following statement: "Since more elements are determinable as the oxides than as any other compound, the determination as oxide must be the best for most of these elements."

2. Why are not more sulfides used as weighing forms?

3. According to the outline given, list the important specific sources of error in one of the following determinations: 10.1, 13.1, or 13.2. For each error, decide (a) whether it is predominantly random or determinate; (b) its sign, if determinate; (c) techniques for its minimization.

Experiment 13.1

1. List some materials for which chloride analysis might be important at some stage in their production, consumption, or study.

2. In bringing Gooch crucibles to constant weight, why is water passed through them before each heating?

3. The AgCl probably contains coprecipitated AgNO₃, since the latter salt is in excess in the mother liquor. Explain the mechanism of washing with dilute HNO₃.

4. Write a reaction showing how AgCl might be reduced to metallic Ag during ignition on filter paper.

5. If the reduction of AgCl by light occurs in contact with the mother liquor, what governs the upper limit of error due to this reduction?

6. In the determination of Ag by precipitation of AgCl with excess NaCl, describe the error due to photodecomposition of the AgCl in contact with the mother liquor.

7. Explain the chemistry of the tests for completeness of precipitation and of washing.

8. What principal processes occur during digestion of the AgCl?

9. Explain why heating a solid to its melting point dries it efficiently. Why is this technique not always used?

10. In terms of the nature of the AgCl precipitate, explain why rinsing with acetone and air-drying might not be effective in removing the last traces of water.

11. Explain how each of the following mistakes would probably affect the result in the gravimetric determination of chloride, assuming that no other mistakes are made. (a) A very high concentration of excess AgNO₃ in the mother liquor. (b) Boiling the solution before or during precipitation of AgCl. (c) Failure to dry the original sample completely. (d) Failure to dry the AgCl completely. (e) Loss of asbestos fibers from the filtering crucible during filtration of AgCl. (f) Use of 34.543 as the atomic weight of Cl. (g) Erroneously recording the weight of a 0.3101-g sample as 0.3011 g.

12. Describe the simplest method you can devise to determine approximately the proper sample size and the proper amount of AgNO₃ precipitant to use, if the Cl content of the sample is not given.

13. Outline, with chemical equations, procedures for determining Cl in each of the following mixtures containing approximately equimolar amounts of both components: (a) NaCl, Na₂S. (b) NaCl, Na₂CO₃. (c) A concentrated solution of SnCl₄ in HCl. (d) NaCl, Na₂SO₃. (e) FeCl₃, CuSO₄.

Experiment 13.2

1. What assumptions are made in drying the sample in this experiment? How could the validity of these assumptions be simply checked?

2. Using ionic equations, explain the chemistry of the tests for completeness of precipitation and of washing.

3. Describe the effect of each of the following mistakes on the result in the analysis for sulfate as BaSO₄. (a) Precipitation in a strongly acid solution. (b) Precipitation in a basic solution. (c) Reduction to BaS during ignition. (d) Acidification with HNO₃ instead of HCl. (e) Erroneously recording the weight of a 19.2735-g crucible as 19.2235 g.

4. Which of the following acids could be most safely used to acidify the solution prior to precipitation of BaSO_4 : H_2SO_4 , HCl , HNO_3 , $\text{HC}_2\text{H}_3\text{O}_2$?

5. A sample of Na_2SO_4 also contains $\text{Fe}_2(\text{SO}_4)_3$. In which case would ferric salts be most extensively coprecipitated with BaSO_4 —by adding the sample to a solution of the BaCl_2 precipitant, or vice versa?

6. Suppose that $\text{Fe}_2(\text{SO}_4)_3$ is coprecipitated with BaSO_4 in the determination of sulfate as BaSO_4 . What happens on ignition? Is the error positive or negative?

7. A sample to be analyzed for sulfate contains $\text{Fe}_2(\text{SO}_4)_3$. Fe^{3+} is to be removed as $\text{Fe}(\text{OH})_3$. Explain why the coprecipitation and loss of sulfate by carrying on the $\text{Fe}(\text{OH})_3$ is quite severe at low pH, but is considerably reduced if $\text{Fe}(\text{OH})_3$ is thrown down by a large excess of NH_3 (S36).

8. Before iron is removed as $\text{Fe}(\text{OH})_3$ to prevent coprecipitation with BaSO_4 , it is desirable to add an oxidizing agent to oxidize all iron completely to the trivalent state, since $\text{Fe}(\text{OH})_3$ is less soluble than $\text{Fe}(\text{OH})_2$. Which of the following oxidants would be most acceptable for this process and why: bromine, KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, HNO_3 ?

9. Sulfate is to be determined as BaSO_4 in a solution containing Ca at a concentration that does not exceed the solubility product of CaSO_4 . BaSO_4 and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ are not isomorphic. Explain how Ca might be carried on the BaSO_4 .

PROBLEMS

Section 13A

1. A sample yields 0.0863 g Zn by an electrolytic method of analysis. How many grams of $\text{ZnHg}(\text{SCN})_4$ could have been obtained? *Ans.* 0.658 g.

2. Set up an arithmetical expression for calculating the % $\text{Ba}_3(\text{PO}_4)_2$ in a sample, S g of which yield W g BaCrO_4 upon gravimetric analysis of the sample for phosphate.

3. A 1.7000-g sample of an iron ore gave a mixture of oxides which upon ignition weighed 0.8432 g. Analysis of the oxide mixture showed that it contained 3.25% Al and 1.83% Ti. Assuming that only Al_2O_3 , TiO_2 , and Fe_2O_3 were in the residue, calculate the percentages of Al, Ti, and Fe in the ore.

Ans. 1.61% Al; 0.91% Ti; 31.51% Fe.

4. A 2.476-g sample of a silicate rock gave 0.3521 g of KClO_4 on analysis for K. Calculate the K content of the rock as % K_2O .

5. One gram of a certain sample gives a certain weight of the nickel salt of dimethylglyoxime. How many grams of the same sample are required to give the same weight of Ni by electrodeposition? *Ans.* 4.922 g.

6. In Table 13.1 (p. 212) find those weighing forms that have the highest and lowest gravimetric factors for converting weight of weighing form to weight of sought-for element.

Experiment 13.1

1. A 0.3652-g sample contains 40–60% Cl. What volume of 0.50 M AgNO_3 should be used as a precipitant, allowing for a 10% excess? *Ans.* 13.6 ml.

2. What weight of AgNO_3 is required theoretically to react with 0.26 g NaCl?

3. A sample contains 20–30% KClO_3 . What weight should be taken in order to give at least 1.0 g AgCl , after reduction? *Ans.* 4.3 g.

4. What weight of pure AgNO_3 is required just to precipitate the Cl in a 0.9350-g sample containing 30.0% NaCl and 70.0% $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$?

5. A sample containing 30.0% NaCl and 40.0% KCl weighs 0.2560 g. What weight of AgCl may be obtained from this sample? *Ans.* 0.3852 g.

6. A 1.0345-g sample of soluble chlorides gave 1.4275 g AgCl. Calculate the Cl content as % Cl and also as % CaCl₂.

7. A sample of pure KClO₃ was reduced to chloride, and the latter determined as AgCl. If 0.893 g AgCl was obtained, what was the weight of KClO₃ in the sample?

Ans. 0.764 g.

8. A 0.8652-g sample of an Ag-Cu alloy is dissolved and analyzed for Ag. If 0.6580 g AgCl is obtained, what is the % Ag in the alloy?

9. Calculate the chemical factor that should be used in converting a known weight of AgCl into an equivalent weight of CaCl₂·2H₂O.

Ans. 0.51291.

10. A precipitate of AgCl weighing 1.000 g is washed with 500 ml of 0.010 M HNO₃.

(a) Calculate the solubility loss in milligrams and in percentage if the washing occurs at 25°C. (b) What minimum weight of AgCl must be formed if the solubility loss of part a must represent less than 0.10% relative error? (c) Repeat parts a and b for a washing at 90°C. See page 162 for solubility data.

11. If an AgCl precipitate is reduced in drying so that it contains 0.70% Ag, what is the relative error in the % Cl calculated from the weight of precipitate?

Ans. -0.23%.

12. On standing in the laboratory locker, an AgCl precipitate is exposed to H₂S so that 1.0% of the AgCl is changed to Ag₂S. (The HCl formed volatilizes.) What is the relative error in the % Cl calculated from the weight of the final precipitate?

Experiment 13.2

1. Calculate the volume of 0.50 M BaCl₂ required just to precipitate the sulfate in 0.25 g Na₂SO₄. What weight of BaSO₄ will be obtained?

Ans. 3.5 ml, 0.41 g.

2. Calculate an upper limit to the volume of BaCl₂ required for this experiment, assuming that a 10% excess is used.

3. Assuming that the sample may range from pure Na₂SO₄ to pure K₂SO₄, calculate an appropriate range of sample sizes to give 0.70–1.00 g BaSO₄.

Ans. 0.52–0.61 g.

4. Calculate chemical factors for transforming the weight of BaSO₄ obtained to weights of the following substances in the original sample: (a) K₂SO₄, (b) K₂S₂O₃, after oxidation to sulfate.

5. A 0.3315-g sample, after treatment to convert all S to sulfate, gives 0.493 g BaSO₄. Calculate the S content of the sample as S, FeS₂, Al₂(SO₄)₃, and SO₃.

Ans. 20.43% S.

6. From the following analyses, calculate the formula of a sulfide mineral: 1.500 g of sample gave 0.5181 g Cu; 1.0000 g of sample gave 0.3050 g Fe; 0.4000 g of sample gave 1.0180 g BaSO₄. Check to find if there are any other constituents in the sample.

7. It is desired to determine Ca by precipitation as CaSO₄, using sample sizes that will yield about 1 g CaSO₄. (a) To keep the loss due to solubility in 100 ml of mother liquor below 3.0 mg CaSO₄, what would have to be the excess sulfate concentration? (b) After excess sulfate is washed out, how much pure wash water could be used, if solubility losses are to be kept below 7.0 mg CaSO₄?

Ans. (a) 0.0052 M; (b) 47 ml.

8. In the determination of sulfate as BaSO₄, 0.8000 g of the ignited precipitate is found to contain 7.0 mg of coprecipitated Na₂SO₄. (a) What is the percentage error of the determination? (b) What is the percentage error of the determination if, in addition, the precipitate contains 3.0 mg of coprecipitated BaCl₂?

14 THE GENERAL METHOD OF VOLUMETRIC ANALYSIS

14A. THE VOLUMETRIC PROCESS

14A.1. Reactions Suitable for Volumetric Analysis

In *volumetric analysis* the sought-for substance is made to react by a *titration* technique with a measurable volume of a reagent *standard solution* of known concentration. When the reaction is complete, the amount of sought-for substance is calculated from the amount of standard reagent used. Relatively few chemical reactions are suitable for volumetric methods. An ideal titration reaction should meet the following requirements. (1) The reaction should go to completion according to a single, well-defined chemical equation; otherwise there is no basis for calculating the amount of sought-for substance from the amount of standard reagent used. (2) An *indicator* must be available to show when the sought-for substance has been consumed, and when an amount of reagent chemically equivalent to the sought-for substance has been added. An indicator may be a substance that changes color or precipitates abruptly at this equivalence point.* (3) The reaction should be rapid and reversible. If it is not rapid, too long a time is required for complete reaction after each increment of standard solution is added to the sought-for substance. If it is not reversible, the indicator change is not sharp. (4) The standard solution should be easy to prepare and simple to use. It should be stable so that frequent redetermination of the concentration is not necessary.

* There often are sharp changes in certain properties of the solution as the equivalence point is passed, and observance of any one of these properties (such as conductance, electromotive potential, or acidity) may indicate the equivalence point.

The neutralization of a strong base with a strong acid is an example of a good volumetric reaction. The neutralization is rapid and complete, and there are no side reactions. The acidity changes sharply as the equivalence point is passed, and this change may be observed in many ways; the use of an acid-base indicator is only one possibility. Both acid and base standard solutions are easy to prepare, and keep well with simple precautions.

The titration of a metal salt (e.g., AlCl_3) with standard base is an example of a poor reaction. The reaction does go to completion because of the insolubility of the $\text{Al}(\text{OH})_3$ formed, and an acid-base indicator can be used to mark the equivalence point. Furthermore, the standard base is stable and easy to use. But the reaction does not proceed according to a single equation, since basic salts are formed, and since there is adsorption and coprecipitation by the gelatinous $\text{Al}(\text{OH})_3$. These side reactions are slow, and the acidity does not reach a steady state for some time after each addition of standard base, especially in the region of the equivalence point.

The four requirements listed above are seldom perfectly realizable. However, shortcomings in some of these requirements may be occasionally surmounted by proper choice of conditions and procedure. In illustration: (1) A reaction may not be as complete as desired at the equivalence point, but by proper choice of conditions and indicator it may still be possible to locate the equivalence point precisely enough for the purpose at hand. The titration of a weak acid with a standard strong base serves as an example. (2) Side reactions may sometimes be made negligible by a proper choice of conditions. As an example, CrCl_2 is a very good standard reducing substance, even though it is oxidized by air. By carrying out the titrations under CO_2 , the air-oxidation is avoided. (3) Even if side reactions cannot be repressed completely, it may be possible to make them occur reproducibly by careful work, so that a reliable correction may be applied to the result. A correction may also be applied if a perfect indicator is not available, and if the best indicator changes at a point somewhat different from the sought-for equivalence point. (4) Sometimes the rate of a slow reaction may be increased with a catalyst, as in the titration of H_3AsO_3 with standard KMnO_4 and a trace of KI . The technique of back titration may also be used to circumvent this difficulty.

14A.2. Types of Volumetric Reactions

Volumetric analyses are based upon two kinds of chemical reactions, metathetical and redox. In a *metathetical* or ion-interchange reaction, no element changes its valence state. Metathetical reactions may pro-

ceed to completion because of formation of insoluble or undissociated products. Good volumetric methods are based upon the following types of reactions.

Formation of a precipitate: $\text{Ag}^+ + \text{Cl}^- \rightleftharpoons \underline{\text{AgCl}}$

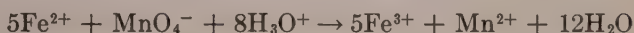
Neutralization: $\text{H}_3\text{O}^+ + \text{OH}^- \rightleftharpoons 2\text{H}_2\text{O}$

Formation of a weak acid: $2\text{H}_3\text{O}^+ + \text{CO}_3^{2-} \rightleftharpoons \text{H}_2\text{CO}_3 + 2\text{H}_2\text{O}$

Formation of an undissociated salt: $\text{Hg}^{2+} + 2\text{Cl}^- \rightleftharpoons \text{HgCl}_2$

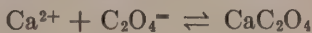
Formation of a complex ion: $\text{Ag}^+ + 2\text{CN}^- \rightleftharpoons \text{Ag}(\text{CN})_2^-$

In *redox* reactions the reacting substances undergo changes in oxidation number. A redox reaction goes to completion if one of the reagents is a strong oxidizer and the other a strong reducer. As an example, Fe^{2+} may be determined by titration with standard KMnO_4 .

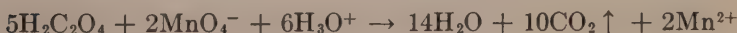
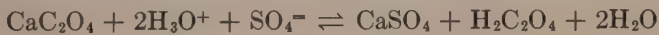


14A.3. Direct and Indirect Methods

The above equations are all examples of direct methods, in which the sought-for substance is titrated directly to the equivalence point with the standard solution. However, for some substances there are no good direct methods, and it is necessary to determine such substances indirectly. An example of an indirect method* is the permanganimetric determination of Ca^{2+} . The Ca^{2+} is mixed with an (unmeasured) excess of $(\text{NH}_4)_2\text{C}_2\text{O}_4$, and time is allowed for complete precipitation.



The CaC_2O_4 is filtered off, washed free from excess oxalate, dissolved in H_2SO_4 , and the resulting $\text{H}_2\text{C}_2\text{O}_4$ titrated with standard KMnO_4 .



Examination of the balanced equations reveals that $1\text{Ca}^{2+} = 1\text{CaC}_2\text{O}_4 = 1\text{H}_2\text{C}_2\text{O}_4 = \frac{2}{5}\text{MnO}_4^-$. Hence for every mole of standard KMnO_4 used in the titration there must have been $\frac{5}{2}$ moles of Ca^{2+} in the original sample. In this indirect method the standard KMnO_4 does not react at all with the sought-for Ca^{2+} , but with a product ($\text{H}_2\text{C}_2\text{O}_4$) of the

* These indirect methods bear no relation to the indirect gravimetric methods of Sec. 9D (p. 145).

reaction between the sought-for Ca^{2+} and another substance. The direct titration of Ca^{2+} with standard oxalate cannot be performed, because there is no indicator and because CaC_2O_4 precipitates too slowly.

The use of such indirect methods greatly extends the number and kinds of determinations that may be performed with a particular standard solution. Study of Table 20.3 (permanganimetric determinations, p. 456) verifies this statement.

14A.4. Comparison of Volumetric and Gravimetric Methods

Compared with gravimetric methods, the advantages of volumetric methods generally outweigh the disadvantages greatly. Whenever a choice is possible, a volumetric analysis is generally preferred over a gravimetric one. The volumetric method is probably used more frequently than any other method for ordinary chemical analysis at the 0.1% error level.

Advantages

1. Volumetric techniques are inherently simpler than gravimetric ones, because the operations of isolation, drying, and weighing a precipitate are not encountered. This simplicity results in speed and ease of analysis. Also, it is axiomatic that the simpler a procedure and the fewer the number of operations involved, the smaller are the chances for accidental error. Also, it is easier to determine and apply reliable corrections for a simple volumetric method than for a relatively more complex gravimetric one.

2. In some cases, volumetric methods are less susceptible to interferences. For example, contamination of a reaction product causes no error, unless the contaminant contains the sought-for or standard substance. Thus silica causes error in the gravimetric determination of Ca as CaC_2O_4 , but causes no error in the permanganimetric determination described above. The gravimetric determination must therefore be preceded by a troublesome separation of silica, but this is unnecessary for the volumetric analysis.

3. By using standard solutions of different concentrations, the volumetric method may be more easily accommodated to a large range of sample sizes. Thus if the amount of sought-for substance is small, a dilute standard solution may be used for titration; if large, a more concentrated solution may be used. There are, of course, limitations upon the concentration at which a given titration may be carried out. As solutions become more dilute, reactions generally become less complete and less rapid, end points become more diffuse, and corrections due to indicator and other errors become relatively larger and less reliable.

For conventional volumetric analysis, about 0.1 *M* standard solutions are generally used; concentrations outside the range 0.001–1 *M* are seldom encountered.

The volumetric method is preferable to the gravimetric for analysis of small samples. For instance, a sample containing 6 mg NaCl would require for titration about 10 ml of 0.01 *M* AgNO₃. This titration could be performed in the ordinary manner, with an error of only a few tenths of a per cent. This accuracy could not be achieved by the ordinary gravimetric method, since only about 15 mg of AgCl would be formed.

Disadvantages

1. The gravimetric method is more precise and accurate for ordinary amounts of sought-for substance (0.1–1 g).

2. Because of the ease in correcting or compensating for error in volumetric methods, there are more empirical, nonstoichiometric volumetric methods than gravimetric ones. Although there is no harm in using such procedures, it must repeatedly be ascertained that the corrected or compensated errors are under control during analysis.

3. If it is desired to base a determination on a reaction that is not complete, an excess of reagent may be used in gravimetric analysis to force the reaction toward completion. This cannot be done in a direct titration, for the titration must be stopped when the reagent added is equivalent to the sought-for substance. Only by the more troublesome procedure of back titration may an excess of reagent be used.

14A.5. General Procedure in Volumetric Determination

Preparation of the standard solution. The most accurate and convenient way of preparing a standard solution is to dissolve a weighed amount of a primary standard substance and to dilute to a measured volume, thus permitting the concentration to be precisely calculated. A measured weight of a *primary standard substance* may be assumed to contain a known weight of that substance. There are not many such substances, since a good primary standard should (1) be easy to obtain, purify, and dry; (2) be easy to test for impurities and to assay; (3) be stable in air under ordinary conditions, at least during weighing, and over longer periods if possible, so that it may be stored; (4) have a high equivalent weight, so that weighing errors may be negligible; (5) react with the desirable characteristics given on page 229. Some primary standard substances are listed in Appendix IVA.

More often, if the reagent is not a primary standard, a *secondary standard solution* must be prepared. The reagent is dissolved and made

up approximately to the concentration desired, and then standardized in one of several ways: (1) The solution may be titrated against a measured weight of a primary standard substance or against a measured volume of a primary standard solution. This is generally the most accurate method of standardization. (2) The solution may be standardized by titration against another reliably known secondary standard solution. (3) The solution to be standardized may be analyzed for the reagent substance by any other method sufficiently accurate for the purpose at hand. For instance, gravimetric determination of the chloride content as AgCl is sometimes used to standardize NaCl or HCl solutions very accurately.

There are other ways of preparing standard solutions. Sometimes quantitative dilution of a standard solution on hand may give a solution of the desired concentration. Many chemical distributors furnish sealed vials containing accurately measured quantities of various reagents, and standard solutions may be obtained by diluting the contents as specified.

Once prepared, standardized, and properly stored, a batch of standard solution suffices for titrating many samples. In spite of all precautions, some standard solutions change during storage and must be restandardized frequently.

The accuracy of standardization is worthy of considerable discussion. Ideally, a standard solution should be known with greater certainty than is desired in analysis of the sample, so that the error in standard solution concentration can only contribute negligibly to the over-all error of the sample analysis. Certainly it is important to realize the uselessness of titrating unknown samples before checks within the required precision are obtained in standardization. If adequate checks cannot be obtained, the sources of error should be sought and corrected before analysis of the samples is begun.

For any solution, several methods of standardization usually exist. It is best to choose a method chemically similar to that intended for the unknown sample, and to carry out standardization and analysis in as similar a manner as possible, so that any determinate errors in standardization and analysis compensate and cancel each other. Thus in the iodimetric determination of Cu in an ore, the $\text{Na}_2\text{S}_2\text{O}_3$ titrant is often standardized with primary standard electrolytic Cu . The titer method of analysis (p. 238) provides such compensation, since the standard solution is standardized with a known amount of the sought-for substance.

Preparation of the sample. Sample preparation includes sampling, weighing, dissolution, and removal of interferences, and is outlined in an elementary way in Chapter 2. For ordinary volumetric analysis with a

50-ml buret, the sample size should be chosen to require around 40 ml of standard solution for titration, so that reading errors are negligible.

In preparing the sample, the analyst has the choice of preparing individual samples for each titration, or of preparing a single, large, master sample, diluting it accurately to a known volume, and taking aliquot parts for each titration. To save time and effort, the aliquot procedure is preferable. If, however, an accidental error is made in preparing the master sample, this error is not revealed by the aliquot procedure. All titrations on the aliquots are affected in the same way by this error, and good checks may still be obtained. The comparative precision of the preparation and titration steps determines the proper choice of procedure. If the standard deviation of the preparation process is considerably greater than that of the titration, then, for maximum precision, the effort should go into preparation of several samples, rather than into titration of several aliquots on a single prepared sample; this is the usual practice. In the rare instances when the standard deviation of the titration process is considerably greater than that of sample preparation, the aliquot procedure is preferable.

Titration of the sample. The time required for the titration itself is usually short compared to that for preparation of the standard solution and sample. Therefore, performance of replicate titrations on aliquots of a single sample should not be shunned, if this significantly decreases the standard deviation of the analysis.

Computing and reporting the result. Volumetric computations are described in the following section. For student work, it is desirable to report standardization data, as well as data on sample analysis, so that the instructor may check computations rather completely if necessary.

14B. COMPUTATIONS OF VOLUMETRIC ANALYSIS

14B.1. Expressing Solution Concentrations

A concentration expresses the amount of solute per unit amount of solution or solvent. There are many ways in which concentration may be expressed, but, if the fundamental concept of concentration is understood, interconversion of these ways is a matter of simple arithmetic. Molarity, normality, and titer are *volume concentration* units, expressing the amount of solute per unit volume of solution, and are used most frequently by analysts. Molarity, normality, and titer are defined more completely in the following sections. *Weight concentrations* are another class of units, expressing the amount of solute per unit weight of solution (or solvent). For example, the weight percentage (grams of solute per 100 g of solution) is sometimes used by manufacturers to give the com-

position of concentrated solutions. To interconvert weight and volume concentrations, the solution density must be known.

Illustrative examples involving different concentration units are given in Sec. 14B.2 (p. 239).

14B.1a. Molarity. The molarity or molar concentration, M , is the number of moles of solute per liter of solution.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{liters of solution}} = \frac{\text{millimoles of solute}}{\text{milliliters of solution}} \quad (14.1)^*$$

The mole and molarity are much used in volumetric calculations. They are unambiguous terms, independent of the particular reaction that the solute undergoes in titration. This is not always true of concentration units like normality and titer, as shown in the following sections.

A word about *milli-units* is in order at this point. In titrations, where rather small fractions of a liter are used, it is slightly more convenient to think in terms of milliliters, milligrams, and millimoles (1 mmole = 0.001 mole), rather than in terms of liters, grams, and moles. The use of milli-units is entirely a matter of personal preference. In this text, milli-units will be used predominantly henceforth.

* By now, the concept of the mole should be as familiar to the student as the concept of the gram.

$$\text{Moles} = \frac{\text{grams}}{\text{molecular weight}} \quad (9.1)$$

Combining Eqs. 9.1 and 14.1 allows the following definition of molarity:

$$\text{Molarity} = \frac{\text{grams of solute}}{(\text{liters of solution}) \times (\text{molecular weight of solute})} \quad (14.1a)$$

Superficially, it might seem advantageous to adopt Eq. 14.1a as the working definition of molarity, since weights are usually given in grams and since grams may be more familiar than moles to the student. There is no fundamental difference between Eqs. 14.1 and 14.1a; the operations in using them are the same, and what may be calculated with the one equation may also be calculated with the other. However, Eq. 14.1a possesses a subtle and important disadvantage if improperly used. The difference between these two equations is in the mode of thinking when they are being used. The user of Eq. 14.1 thinks in terms of moles, whereas the user of Eq. 14.1a is likely to think in terms of grams. Note that molarity may be calculated with Eq. 14.1a without the user's having the slightest idea of what a mole is! If Eq. 14.1a is favored in order to avoid exercising the mole concept, this equation should be abandoned. Since the mole concept is indispensable to chemical reasoning, Eq. 14.1 is recommended over 14.1a.

The unwitting use of equations like 14.1a in an evasive sense is probably by far the most important root of trouble among students who find it difficult to understand and use simple chemical concepts. The student must constantly strive to keep from falling into this way of thinking, for it is the easiest way at the beginning of study; its disadvantages do not become apparent until later, when the student attempts to use or to extend his knowledge.

14B.1b. Normality. The neutralization* *equivalent weight*, or simply *equivalent*, is the number of grams of a substance required to react with, replace, or furnish one mole of H_3O^+ or OH^- . In general, there are η equivalents per mole, where η is the number of H_3O^+ or OH^- replaced by, furnished by, or reacting with one molecule of the substance. Since η is always a small whole number, the equivalent weight is always equal to the molecular weight or a fraction of it.

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{\eta} \quad (14.2)$$

The number of equivalents in any number of grams of a substance is

$$\text{Equivalents} = \frac{\text{grams}}{\text{equivalent weight}} \quad (14.3)$$

The normality or normal concentration, N , is the number of equivalents of solute per liter of solution.

$$\text{Normality} = \frac{\text{equivalents of solute}}{\text{liters of solution}} = \frac{\text{milliequivalents of solute}}{\text{milliliters of solution}} \quad (14.4)$$

The terms "equivalents" and "normality" tend to be ambiguous, because some substances may react with or furnish H_3O^+ or OH^- in more than one way. In order that equivalents and normality may make

TABLE 14.1

RELATIONS AMONG MOLES, EQUIVALENTS, MOLARITY, AND NORMALITY
FOR VARIOUS SUBSTANCES

Substance	Reaction	Equivalents per Mole	1 M Solution Is
HCl.....	$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$	1	1 N
H_2SO_4	$\text{H}_2\text{SO}_4 + 2\text{NaOH} \rightarrow 2\text{H}_2\text{O} + \text{Na}_2\text{SO}_4$	2	2 N
Na_2CO_3	$\text{Na}_2\text{CO}_3 + \text{HCl} \rightarrow \text{NaHCO}_3 + \text{NaCl}$	1	1 N
Na_2CO_3	$\text{Na}_2\text{CO}_3 + 2\text{HCl} \rightarrow 2\text{NaCl} + \text{H}_2\text{O} + \text{CO}_2 \uparrow$	2	2 N
H_3PO_4	$\text{H}_3\text{PO}_4 + \text{NaOH} \rightarrow \text{NaH}_2\text{PO}_4 + \text{H}_2\text{O}$	1	1 N
H_3PO_4	$\text{H}_3\text{PO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2\text{HPO}_4 + 2\text{H}_2\text{O}$	2	2 N

sense, the chemical equation by which the substance reacts must be explicitly stated, understood, or derivable from the context. Table 14.1 should help to clarify the definitions of equivalent weight and normality. It should be noted that the term "1 N Na_2CO_3 " out of context is am-

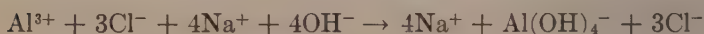
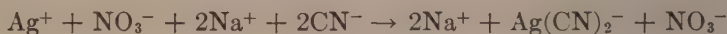
* This modifier, omitted henceforth, is to emphasize the difference between these equivalent weights and the redox equivalent weights encountered in Chapter 19.

biguous, for it may mean either 0.5 *M* or 1 *M*, depending on the reaction that the Na_2CO_3 undergoes; only when a particular reaction is associated with this term does it have definite meaning.

In volumetric analysis, equivalents and normality are more frequently used than moles and molarity. The usefulness of the first two terms lies in the fact that one equivalent of a sought-for substance always requires for titration one equivalent of the standard reagent; this allows computations without the necessity of writing the chemical equations for the reactions involved in the determination. At the equivalence point of a titration,

$$\left(\begin{array}{c} \text{Equivalents of} \\ \text{sought-for substance} \end{array} \right) = \left(\begin{array}{c} \text{equivalents of} \\ \text{standard reagent} \end{array} \right) \quad (14.5)$$

The concepts of equivalent weight and normality are sometimes applied to salts when the metathetical reactions do not involve H_3O^+ or OH^- . In such cases, the number of equivalents per mole is the number of positively (or negatively) charged ions per molecule that could be replaced with H_3O^+ (or OH^-), if desired. Thus a 1 *M* AgNO_3 solution is often called 1 *N*, and a 1 *M* AlCl_3 solution is often called 3 *N*. This practice is not recommended, for the salt may not show this number of equivalents in the titration, which will cause trouble in reactions* like the following:



Such ambiguities and confusion do not arise when moles and molarities are used, since these terms are defined independently of any chemical reactions.

14B.1c. Titer. The titer of a solution is the weight of a substance equivalent to a unit volume of the solution. The substance need not be the solute substance itself, but may be a sought-for substance titrated by the solution, or a substance derivable from the solution.

$$\text{Titer} = \frac{\text{grams of substance}}{\text{liters of solution}} = \frac{\text{milligrams of substance}}{\text{milliliters of solution}} \quad (14.6)$$

The titer is a volumetric chemical factor, with which the amount of sought-for substance may be directly calculated from the volume of standard solution required for its titration, without any consideration

* Accurate titrations for Ag^+ , CN^- , and Al^{3+} are based on these reactions.

or knowledge of the chemical processes that occur in the analysis. The titer method of computation is useful as a time-saver in routine calculations, and in teaching unskilled help how to compute the results of a titration without teaching the associated chemistry. But in studying chemical principles, the titer method should not be overemphasized.

Empirical methods require the use of titer values. The titer value of the standard solution is determined by titration against a known weight of the sought-for substance, and then unknown samples are titrated by the same procedure. The advantage of performing analyses in this way is that determinate errors tend to cancel each other. However, the titer method is not a panacea for the elimination of errors, and its limitations should be understood. It significantly reduces only reproducible errors that occur in both the standardization and the analysis.

14B.2. Illustrative Examples

The following examples are representative of calculations encountered in volumetric analysis. They also outline the usual ways of preparing, standardizing, and titrating solutions. These examples should be studied to find how the fundamental equations of this chapter are applied, but should not be memorized as important types of problems.

Example 1. *Preparation of a Standard Solution from a Primary Standard Substance.* How much primary standard potassium acid phthalate ($\text{KHC}_8\text{H}_4\text{O}_4$ or KHP) is required to prepare 998.2 ml of 0.1000 *N* solution?

If regular units are used,

$$0.1000 \left| \begin{array}{l} \times \frac{998.2}{1000} \\ \text{eq KHP/l} \end{array} \right| \times 204.23 = 20.38 \text{ g KHP}$$

— eq KHP required for 998.2 ml

If milli-units are used,

$$0.1000 \left| \begin{array}{l} \times 998.2 \\ \text{meq KHP/ml} \end{array} \right| \times 204.23 = 2.038 \times 10^4 \text{ mg KHP}$$

— meq KHP required for 998.2 ml

Example 2. *Preparation of a Standard Solution by Dilution of a Known Standard Solution.* What volume of 0.2963 *M* H_2SO_4 is required to prepare 250.0 ml of 0.1000 *N* H_2SO_4 ?

$$0.1000 \left| \begin{array}{l} \times 250.0 \\ \text{meq H}_2\text{SO}_4/\text{ml of 0.1000 N solution} \end{array} \right| \times \frac{1}{2} \left| \begin{array}{l} \times \frac{1}{0.2963} \\ \text{mmoles H}_2\text{SO}_4 \text{ required} \\ \text{ml of 0.2963 M H}_2\text{SO}_4 \text{ required} \end{array} \right| = 42.19 \text{ ml}$$

Example 3. *Preparation of a Standard Solution of Approximately Known Concentration.* What volume of concentrated HCl is required to prepare a liter of approximately 0.100 *N* solution?

$$0.100 \times 36.46 \times \frac{100}{38.0} \times \frac{1}{1.188} = 8.1 \text{ ml}$$

↑ Density of conc. HCl (Appendix IVB).
g conc. HCl (38.0% by weight, Appendix IVB)
required

— g pure HCl required

— eq pure HCl required for 1 l

Example 4. *Standardization of a Solution against a Primary Standard Substance.* What is the normality of the HCl of Ex. 3, if 45.23 ml are required to titrate a 0.2505-g sample of Na_2CO_3 according to the reaction



$$\frac{250.5}{105.99/2} \times \frac{1}{45.23} = 0.10451 \text{ N}$$

— meq HCl/ml

— meq Na_2CO_3 , or meq HCl in 45.23 ml

Example 5. *Standardization of a Solution against Another Standard Solution.* What is the normality of an HCl solution, a 25.03-ml portion of which requires 29.09 ml of 0.1025 *N* NaOH for titration?

HCl solution is 29.09/25.03 times as concentrated as the NaOH.

$$\text{HCl normality} = 0.1025 \times \frac{29.09}{25.03} = 0.1191 \text{ N}$$

Example 6. *Gravimetric Standardization of a Solution.* What is the normality of an H_2SO_4 solution, 100.2 ml of which yield 0.2976 g BaSO_4 ?

$$\frac{297.6}{233.40} \times \frac{1}{100.2} \times 2 = 0.02545 \text{ N}$$

— meq H_2SO_4 /ml

— mmoles H_2SO_4 /ml

— mmoles BaSO_4 , or mmoles H_2SO_4 in 100.2 ml

Example 7. *Selection of Sample Size to Give Proper Titration Volume.* An Na_2CO_3 -NaCl sample contains 40–60% Na_2CO_3 . What sample size should be taken so that as much 0.1050 *N* acid is required in titration as possible, but not more than 50 ml? Assume two equivalents per mole of Na_2CO_3 .

This means that a 60% sample should use 50 ml of acid.

$$0.1050 \times 50 \times \frac{105.99}{2} \times \frac{100}{60} = 4.6 \times 10^2 \text{ mg}$$

— mg of 60% Na_2CO_3 required

— mg pure Na_2CO_3 required

— meq acid in 50 ml, or meq Na_2CO_3 required

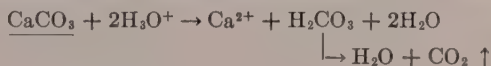
— meq acid/ml

Example 8. *Calculation of the Amount of a Sought-for Substance by Direct Titration.* What is the percentage of acetic acid ($\text{HC}_2\text{H}_3\text{O}_2$) in a vinegar, a 10.00-g sample of which requires 35.27 ml of 0.100 *N* base for titration?

$$0.100 \times 35.27 \left| \times 60.05 \right| \times \frac{100}{10,000} = 2.12\% \text{ HC}_2\text{H}_3\text{O}_2$$

$\underbrace{\hspace{10em}}_{\text{mg HC}_2\text{H}_3\text{O}_2}$
 $\underbrace{\hspace{10em}}_{\text{meq base used, or meq HC}_2\text{H}_3\text{O}_2 \text{ in sample}}$

Example 9. *Calculation of the Amount of a Sought-for Substance by Back Titration.* CaCO_3 , being insoluble, cannot be directly titrated with standard acid. However, an excess of standard acid may be added, whereupon the CaCO_3 dissolves.



The excess HCl left after reaction may be found by a titration with standard base. The difference between the total HCl added and the HCl left is the HCl that reacts with the CaCO_3 .

A sample of CaCO_3 is treated carefully with 50.05 ml of 0.1025 *N* HCl. The CO_2 is boiled off, the solution cooled, and the excess HCl titrated with 0.1097 *N* base, 5.23 ml being required. What is the weight of CaCO_3 in the sample?

$$\begin{aligned} \text{meq CaCO}_3 &= \text{meq HCl reacting with the CaCO}_3 \\ &= \left(\begin{array}{c} \text{total meq} \\ \text{HCl added} \end{array} \right) - \left(\begin{array}{c} \text{meq HCl left, or} \\ \text{meq base used} \end{array} \right) \\ &= (0.1025 \times 50.05) - (0.1097 \times 5.23) \\ &= 4.556 \text{ meq} \\ \text{mg CaCO}_3 &= 4.556 \times \frac{100.09}{2} = 228.0 \text{ mg} \end{aligned}$$

Example 10. *Data for Combined Standardization and Analysis. Titer versus Normality Methods of Computation.* A 0.1234-g sample of primary standard Na_2CO_3 requires for titration 27.92 ml of an HCl solution, according to the equation on page 231. This HCl solution is then used to titrate the Na_2CO_3 in an Na_2CO_3 -NaCl sample, 48.76 ml being required. What is the weight of Na_2CO_3 in the sample?

Normality method:

$$\begin{aligned} \text{HCl normality} &= \frac{123.4}{105.99/2} \left| \times \frac{1}{27.92} \right| = 0.08339 \text{ N} \\ &\quad \underbrace{\hspace{10em}}_{\text{meq Na}_2\text{CO}_3, \text{ or meq HCl in 27.92 ml}} \\ &\quad \underbrace{\hspace{10em}}_{\text{meq HCl/ml}} \\ \left(\begin{array}{c} \text{mg Na}_2\text{CO}_3 \\ \text{in sample} \end{array} \right) &= 0.08339 \times 48.76 \left| \times \frac{105.99}{2} \right| = 215.5 \text{ mg} \\ &\quad \underbrace{\hspace{10em}}_{\text{meq Na}_2\text{CO}_3 \text{ in sample}} \\ &\quad \underbrace{\hspace{10em}}_{\text{meq HCl used in titration, or} \\ \text{meq Na}_2\text{CO}_3 \text{ in sample}} \end{aligned}$$

Titer method: This is particularly useful here, since the sought-for substance is used in standardization. (However, the titer method is no shorter than the normality method if a substance different from the sought-for one is used in standardization.)

$$\left(\frac{\text{Na}_2\text{CO}_3 \text{ titer of}}{\text{HCl solution}} \right) = \frac{0.1234 \times 1000}{27.92} = 4.420 \frac{\text{mg Na}_2\text{CO}_3}{\text{ml HCl}}$$

$$\left(\frac{\text{wt. Na}_2\text{CO}_3}{\text{in sample}} \right) = 4.420 \times 48.76 = 215.5 \text{ mg Na}_2\text{CO}_3$$

QUESTIONS

Section 14A

1. Explain why the reaction between Ag^+ and Cl^- (p. 231) is suitable for volumetric analysis. What phenomenon might be taken as an indication of the equivalence point? (Consider what happens to each drop of reagent before and after the equivalence point. Answer these questions for the reactions between H^+ and CO_3^{2-} and between Hg^{2+} and Cl^- .)

2. Why is HCl more widely used than HNO_3 as an acidimetric standard solution?

3. Give examples of coprecipitation with CaC_2O_4 that might cause error in the indirect determination of Ca with KMnO_4 .

4. The precipitation of NaCl by AgNO_3 may be made the basis of either a volumetric or gravimetric method for determining chloride. Give an example of an impurity that would cause error in the gravimetric method but not in the volumetric method. Give an example of an impurity that would cause error in both methods. Explain the examples.

5. Explain what difficulties might be encountered if direct titration procedures were based upon the following reactions: (a) $\text{Al}^{3+} + \text{NaOH}$. (b) $\text{H}_2\text{S} + \text{HNO}_3$. (c) $\text{Cu}^{2+} + \text{Na}_2\text{S}$. (d) $\text{CaCO}_3 + \text{HCl}$. (e) $\text{Cu}_{(\text{metal})} + \text{HNO}_3$. (f) $\text{Cu}^{2+} + \text{C}_2\text{O}_4^{2-}$. (g) $2\text{Ag}^+ + \text{SO}_4^{2-}$.

6. What are the objections to titrating with standard solutions that exceed 1 *N* in concentration? If very concentrated solutions must be analyzed, devise a technique that would avoid the use of very concentrated standard solutions.

7. Discuss phenomena that may cause two reagents to react nonstoichiometrically.

8. What must be assumed if an HCl solution is standardized gravimetrically (by conversion of Cl to AgCl), and is then used to titrate basic samples?

9. In the indirect method for determining Ca, describe a variation that involves analysis of the filtrate for excess oxalate. Outline the computations. Compare the advantages and disadvantages of this procedure with that given in the text.

10. Explain how back titration may be used to make a slow (but complete) reaction the basis of a volumetric method. Repeat the explanation for an incomplete reaction.

11. Cite the conditions under which each of the following alternatives would be preferable to the other two: (a) Prepare a single master sample, and titrate 4 aliquots. (b) Prepare 2 master samples, and run 2 titrations on each. (c) Prepare 4 individual samples, and run a single titration on each.

Section 14B

1. Why is the term "1 *N* H_3PO_4 " ambiguous? Modify the term to make it meaningful.

2. Why is the term "1 N CuCl_2 " ambiguous? Modify the term to make it meaningful.
3. How many equivalents are there per mole for AgNO_3 and for AlCl_3 , according to the equations on page 238?
4. What is meant by saying that the Ca titer of a KMnO_4 solution is 1.0 mg/ml?
5. In a titration, what is the relationship between the moles of reagent and the moles of sought-for substance? Between the equivalents?

PROBLEMS

Section 14B

Problems involving moles and molarity may be found in Chapter 4.

1. Give the normalities of the solutions resulting when the following weights of solutes are dissolved in the given volumes: (a) 2.00 g $\text{KHC}_8\text{H}_4\text{O}_4$ in 150.0 ml. (b) 3.83 g $\text{HC}_2\text{H}_3\text{O}_2$ in 225 ml. (c) 5.00 g $\text{Ba}(\text{OH})_2$ in 700 ml. (d) 3.00 g Na_2CO_3 in 249.85 ml. *Ans. (c) 0.0834 N .*
2. How many grams of solute are there in each of the following solutions? (a) 1.500 l of 0.1500 N HCl . (b) 3.50 ml of 0.400 N H_2SO_4 . (c) 21.3 ml of 0.398 M NaCl . (d) 39.2 ml of 0.125 N HClO_4 . (e) 42.7 ml of 0.1900 M H_3PO_4 . (f) 17.8 ml of 0.119 N H_3PO_4 . *Ans. (e) 0.795 g.*
3. What volumes of the following solutions are required to give 2.00 g of each solute? (a) 0.2500 N H_2SO_4 . (b) 0.1920 M NaCl . (c) 0.1008 M AgNO_3 . (d) 0.500 N $\text{HC}_2\text{H}_3\text{O}_2$. (e) 0.0100 N $\text{Ca}(\text{OH})_2$. (f) 0.0893 N $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. *Ans. (f) 178 or 355 ml.*
4. How many milliequivalents of each solute are there in each of the solutions of Prob. 2? *Ans. (e) 8.11, 16.23, or 24.3 meq.*
5. What weight of NaOH is required to neutralize completely each of the acid solutions of Prob. 2? *Ans. (e) 974 mg.*
6. What volume of 0.0926 N base is required to neutralize completely each of the acid solutions in Prob. 2? *Ans. (e) 263 ml.*
7. What volume of each of the solutions of Prob. 2 should be taken to give one liter of 0.0358 M solution? *Ans. (e) 188 ml.*
8. To what volume should each sample of Prob. 2 be diluted to give 0.0500 N solution? *Ans. (e) 162.3, 324, or 487 ml.*
9. To acquire facility with the fundamentals of volumetric analysis, solve the following problems mentally, giving only approximate answers. (a) How many grams of NaOH are in 20 ml of 0.1 N solution? (b) What is the normality of an H_2SO_4 solution that contains 23 g/250 ml? (c) How many equivalents are in 23 ml of 0.15 N solution? (d) How many milliequivalents are in 52 ml of 0.5 N solution? (e) How many milligrams of CaCO_3 are required to neutralize 27 ml of 0.5 N H_2SO_4 ? (f) How many milliliters of 0.25 N NaOH are required to neutralize 58 ml of 0.6 N H_2SO_4 ? (g) What is the MgO titer of 0.1 N H_2SO_4 ? (h) What weight of Na_2CO_3 would require 40 ml of 0.1 N acid for titration to a CO_2 end point? (i) How many milliliters of 0.1 N HCl are equivalent to 0.1 g CaCO_3 ? (j) How many milliliters of 0.1 N HCl are required for 23 meq? *Ans. (b) 2 N .*
10. What is the normality of an HCl solution if a 100.0-ml aliquot yields 0.3075 g AgCl ?
11. What is the normality of an H_2SO_4 solution if a 50.00-ml portion requires 37.83 ml of 0.1105 N base for titration? *Ans. 0.0836 N .*

12. In titrating a 2.50-g sample containing NaOH and NaCl, 42.96 ml of 0.1000 N HCl were added too rapidly, and the equivalence point was overrun. The solution was back-titrated with 0.1152 N NaOH, 3.82 ml being required. What is the % NaOH in the sample?

13. Compute the percentage of Na_2CO_3 in a 1.000-g sample that requires 32.06 ml of 0.1200 N HCl for titration to CO_2 . *Ans.* 20.39%.

14. An NaCl-KCl sample contains 55–60% Cl. (a) What sample size should be taken so that as much 0.1190 M AgNO_3 as possible will be used for titration, but not more than 50 ml? (b) What range of sample sizes should be used in order that 25–50 ml of the standard AgNO_3 will be used in titration?

15. If the AgNO_3 titer of a certain solution is 12.03 mg/ml, what is the KCl titer?

Ans. 5.280 mg/ml.

16. Give the titer values of 0.1000 N HCl in terms of (a) KOH, (b) K_2O , (c) Na_2CO_3 (titration to CO_2), (d) AgNO_3 .

17. What is the AgNO_3 titer of one-tenth molar CaCl_2 solution? What is the CaCl_2 titer of one-tenth normal AgNO_3 solution?

Ans. 33.976 mg/ml; 5.5493 mg/ml.

18. The CaO titer of an HCl solution is 1.000 mg/ml. What is the % CaO in 1.000 g of a CaO- CaCl_2 mixture that requires 37.42 ml of the HCl solution for titration?

19. V ml of N normal standard solution are required to titrate a sample weighing S g. Let E be the equivalent weight of sought-for substance, and P its percentage in the sample. (a) Give an expression for P , and compare with Eq. 9.2 (p. 143). (b) Express the titer of the standard solution in terms of sought-for substance.

Ans. (a) $VNE/(10S)\%$; (b) NE mg/ml.

20. What is the normality as a base of a solution containing 4.30 g CaO and 1.50 g KOH per 100 ml?

21. A "syropy phosphoric acid" sample is analyzed and found to contain 61.45% P_2O_5 , and to have a specific gravity of 1.690. Calculate the volume and weight of this sample required to prepare 1.000 liter of 0.1000 M H_3PO_4 solution.

Ans. 15.95 g; 9.44 ml.

15 VOLUMETRIC APPARATUS AND TECHNIQUES*

15A. APPARATUS

15A.1. Graduated Cylinders

Graduated cylinders are used for approximate measurements, and vary in size from 5 ml to several liters. The standard deviation is about 1% of the maximum volume. It is most accurate to use the smallest cylinder that will hold the volume being measured. Some cylinders are marked to contain (TC) and others are marked to deliver (TD).

15A.2. Pipets

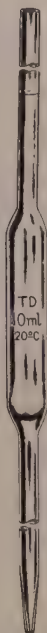
Pipets are used to deliver certain volumes precisely. A transfer pipet (Fig. 15.1) delivers only one certain volume. Ordinary transfer pipets vary in size from 1 to 100 ml. With proper care, the standard deviation of delivery varies from less than 0.01 ml for smaller sizes to only a few hundredths of a milliliter for larger sizes (see the Supplement, p. 746, for further details). Simpler and faster to use than burets, pipets are also easier to clean.

There are many varieties of pipets. Measuring, or graduated, pipets (Fig. 15.1) are less precise than transfer pipets, but they may be used around the 1% error level. Micropipets range from 10 to 100 μ l (1 μ l =

*A 25-minute instructional film on the use of the volumetric flask, pipet, and buret is available from the Television Laboratory, University of Wisconsin, Madison, Wisconsin.



Ordinary buret



Volumetric
or transfer pipet



Volumetric flask



Weight buret



Automatic zero buret
(with two-way stopcock)



Graduated pipet (Mohr)



Microburet with reservoir
and microdrop tip

FIG. 15.1. Volumetric Apparatus (Reproduced by courtesy of E. H. Sargent & Co.)

0.001 ml). They must be calibrated to contain, rather than to deliver, and the contents must be rinsed quantitatively into the delivery vessel, since the ratio of surface to volume is so large that a large fraction of the liquid is retained on the walls. Volumes may be delivered with a standard deviation of about 0.1% for the middle-sized and larger micropipets (K7).

15A.3. Burets

Burets (Fig. 15.1) are graduated pipets equipped with stopcocks to control delivery. Burets used in ordinary volumetric analysis vary in size from 10 to 50 ml. The buret commonly used in student work has a capacity of 50 ml, and is graduated in tenths of a milliliter, so that any volume of 50 ml or less may be delivered with a standard deviation of about 0.01 ml (see the Supplement, p. 746, for further details).

Burets vary in type more than any other piece of volumetric equipment. (1) In capacity, burets may vary from 100 ml down to 25 λ ; the latter size may still be used at the 0.1% error level (K7). (2) Some burets have a two-way stopcock (Fig. 15.1) at the bottom; they deliver through one passage of the stopcock, and are filled through the other passage from a permanently connected reservoir of standard solution. Some burets have the reservoirs permanently built in (Fig. 15.1). There are pipets that are similarly constructed for routine use. (3) Automatic zero burets (Fig. 15.1) are used in routine work to eliminate the necessity of taking zero readings. (4) The Schellbach buret has a vertical blue line on a milky background along the back side. The blue line is optically distorted to a pip by the meniscus, which is thereby marked for more convenient reading than is possible with the ordinary buret. (5) Weight burets (Fig. 15.1) are graduated only roughly, but they are weighed before and after titration, so that the weight of standard solution used is measured, rather than the volume. Since the weight may be obtained with a standard error around 0.1 mg (0.0001 ml), much greater precision may be obtained than with an ordinary buret. Although more troublesome to use, weight burets avoid many of the errors of ordinary burets, since temperature and volume calibration corrections need not be applied.

There are many other kinds of burets for special purposes; the worker should consider the various types available and should choose the one best suited to his problem.

15A.4. Volumetric Flasks

A volumetric flask (Fig. 15.1) is designed to contain precisely one certain volume. Volumetric flasks usually vary in size from a few milli-

liters to several liters. The neck is narrow compared to the body, so that a small error in adjusting the level of the meniscus does not cause appreciable error in the total volume. With proper care, the standard error in a moderate-sized flask is only a few hundredths of a per cent (see the Supplement, p. 746, for further details). There are also micro-volumetric flasks with total capacities of only 0.1 ml and standard errors of only a few tenths of a per cent. Flasks are seldom used to deliver, since their precision is considerably less than when used to contain.

15B. TECHNIQUES

15B.1. Cleaning Volumetric Glassware

A piece of volumetric apparatus is sufficiently clean if its surface is uniformly wetted by distilled water. Oily contamination prevents glass walls from being uniformly wetted; drainage is then uneven and delivery is not precise. A general rule is to clean glassware immediately after use, since it is much more difficult to remove chemicals that have been allowed to cake and age.

15B.1a. Cleaning solutions. Glasses have excellent resistance to acids (except HF). Alkaline solutions etch glass on prolonged contact, and equipment should be rinsed free of such solutions soon after use. Dilute detergent solutions (up to 2%) have no serious effect on glass, unless in contact for long periods, or unless the detergent is allowed to dry on the glass. Abrasive cleaners should never be used, for these soon mar the surface. The resulting scratches prevent proper drainage and provide lodging places for contaminants. The fillers fused into the graduation marks are not as resistant to acids and alkalis as the glass itself, and the graduations should not be immersed for prolonged periods in cleaning solutions.

Except in special instances, all ordinary glassware and volumetric equipment is best cleaned with a warm 1–2% detergent solution. Mechanical action, such as shaking or scrubbing with a bottle brush, increases cleaning efficiency. Sometimes, warm 1–2% Na_3PO_4 (trisodium phosphate) is used.

When detergents and trisodium phosphate are ineffective, *cleaning solution* ($\text{H}_2\text{SO}_4\text{-Na}_2\text{Cr}_2\text{O}_7$) may be used. It is particularly good for the insides of volumetric equipment, where the scouring required for effective detergent action cannot be achieved. It is also useful for cleaning glassware containing deposits of organic materials. Cleaning solution is prepared by adding about 10 g of technical $\text{Na}_2\text{Cr}_2\text{O}_7^*$ to

* $\text{K}_2\text{Cr}_2\text{O}_7$ is less soluble, and cannot be used as a substitute for $\text{Na}_2\text{Cr}_2\text{O}_7$.

about 200 ml of hot (100°C) conc. H_2SO_4 in a large beaker, and stirring for a few minutes to allow the $\text{Na}_2\text{Cr}_2\text{O}_7$ to go into solution. The mixture is then allowed to cool to about 50°C , and is decanted for storage into a 500-ml wide-mouthed glass-stoppered bottle, leaving any undissolved crystals behind. To use cleaning solution, the apparatus should first be rinsed as well as possible with water. The cleaning solution is poured or sucked into the apparatus so as to wet all parts, and is then poured back into the storage bottle. Small articles (stoppers, etc.) are best put in a beaker, so that cleaning solution may be poured over them. The apparatus is left to stand a few minutes (or longer if necessary) to give the cleaning solution time to act, after which excess cleaning solution is poured back into the storage bottle, and the apparatus is rinsed thoroughly with distilled water. Cold cleaning solution is adequate for many purposes, but hot solution is much more effective.

Cleaning solution must be used with great care, since it is extremely corrosive and will destroy clothing before it can be rinsed off. If the smallest drop is spilled on the bench or floor, it must be cleaned up immediately. It should be rinsed off the hands immediately; in the mouth it produces instant and severe burns. Needless to say, safety glasses should always be worn when handling cleaning solution. Spent cleaning solution is greenish (owing to reduction of dichromate) or light orange (owing to dilution with water) and should not be poured back into the storage bottle. Cleaning solution should not be left long in an open container, for it absorbs water from the air and may even overflow after several days if the container is left fairly full.

There are other kinds of cleaning solutions, each useful for certain kinds of contaminants (O1). Burets stained with metallic Ag are easily cleaned with conc. HNO_3 ; MnO_2 stains may be removed with conc. HCl , and so on.

15B.1b. Cleaning techniques. A volumetric flask, pipet, or buret that no longer drains uniformly is first rinsed thoroughly with tap water. The apparatus is then flushed with cleaning solution as described above, the solution being kept away from the stopcocks so that the grease will not be removed. (A procedure for rinsing a buret with cleaning solution is shown in Fig. 15.2.) The cleaning solution is then rinsed out thoroughly with distilled water and the outside of the apparatus is wiped dry. To check cleanliness, the equipment is filled with distilled water and allowed to drain. If the water drains from the inner walls in a uniform film, the apparatus is clean; if the film coalesces into streams or droplets, further cleaning is necessary. After being allowed to drain for a few minutes, the equipment is stored with the inside undried. Burets are best stored in an upright position, filled well above the zero mark with distilled water. If this cannot be done in the restricted

locker space, it is best to rinse again with cleaning solution just before use. Burets stored empty become contaminated with a grease film that spreads from the stopcock.

Equipment that is very dirty must be partially cleaned before being flushed with cleaning solution. Thus equipment that is smeared with stopcock grease, for example, should first be cleaned with benzene or

1. Place inverted buret in beaker containing warm cleaning solution.

2. Open stopcock and apply suction with aspirator bulb, drawing solution up into the buret. Fill almost to stopcock.

3. Close stopcock and allow solution to stand for a few minutes.

4. Open stopcock to allow cleaning solution to drain back into beaker.

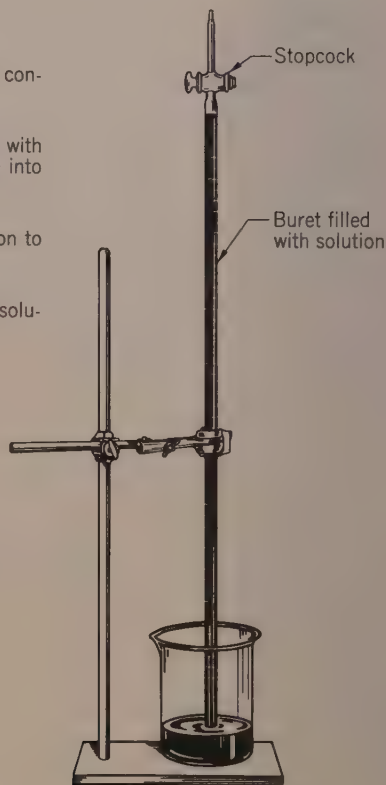


FIG. 15.2. Flushing a Buret with Cleaning Solution

acetone, rinsed with water, then cleaned with a brush and detergent solution, and rinsed again with water. (HAZARD: Keep organic solvents far away from open flames, and do not allow vapors or puddles to accumulate in the sink.) In such cleanings the apparatus is usually disassembled, and stopcocks are removed.

In cleaning a buret the stopcock plug is not removed and cleaned unless necessary. If, however, the stopcock has become unseated or frozen, or if the grease has worked out, removal and cleaning are necessary. The following procedure is suggested.

1. Rinse the equipment as well as possible with tap water, and dry the outside with a towel.

2. Remove the plug. If it is "frozen," the following techniques should be tried in order: (a) Tap the small end of the plug gently, first with a wooden block, and next with a heavy glass stopper or hammer through a few thicknesses of paper or toweling to prevent chipping. The buret should be held in the hand while being tapped. If placed on a nonresilient surface, it may be broken. (b) Soak in a warm trisodium phosphate solution, and then try tapping again. (c) Heat the barrel for a short time directly over a small burner flame, so that it expands, and then try tapping again. (d) Use a stopcock extractor, which either succeeds or breaks the stopcock. Never apply great strength with the hands to turn a frozen stopcock, for breakage and severe cuts may result. Force should be applied with the fingers only through several layers of toweling.

3. After removing the plug, wipe the grease from it and from the inside of the barrel with a rag soaked in benzene. Grease may be removed from the hole in the plug with a pipe cleaner soaked in benzene. The pipe cleaner may also be used to remove grease from the stopcock barrel holes, but any grease in the tip or up in the buret proper may have to be removed by soaking the parts in benzene or by running benzene through them. A fine wire inserted into the tip helps to loosen lumps.

4. Wipe off excess benzene, flush with water, and wash the stopcock parts with warm detergent solution. Then immerse the tip, barrel, and plug in a beaker of warm cleaning solution for a short time.

5. Rinse the buret with tap water, and finally with distilled water, and dry the stopcock barrel and plug with a clean towel. Seat the plug with good stopcock grease* as shown in Fig. 15.3. If this is not done properly, the lubricant may spread and obstruct the holes, in which case the plug must be removed, cleaned, and regreased.

6. Finally, clean the buret proper with cleaning solution, as in Fig. 15.2.

There are some practices that should be avoided in handling volumetric glassware. (1) It is permissible to pour warm solutions into volumetric glassware, but solutions should never be heated directly in the equipment. Not only is there a chance of breakage, but strains may result that will change slowly with time and invalidate calibration. (2) Equipment should not be left immersed in cleaning solutions for prolonged times. (3) It is seldom worth while to dry the insides of glassware rapidly by wiping, air-blowing, or rinsing with acetone.

*Vaseline does not have the body for proper lubricant action. Silicone greases are not recommended for volumetric equipment; they spread quickly into a film that prevents uniform drainage, and which is very difficult to remove.

Compressed air may contain traces of oil, and room air, traces of dust. Acetone, unless of a very good grade, may contain traces of nonvolatile oils. Most glassware may be used wet, after being drained for just a few minutes. On the rare occasions when dry equipment is needed, it should be cleaned sufficiently in advance to permit its draining and drying during storage in the locker. It has been reported that volumetric equipment may be oven-dried without harm (M20). However, special ovens should be set aside and designated for the drying of wet equipment; samples and other chemicals cannot be properly dried in a moisture-laden atmosphere.

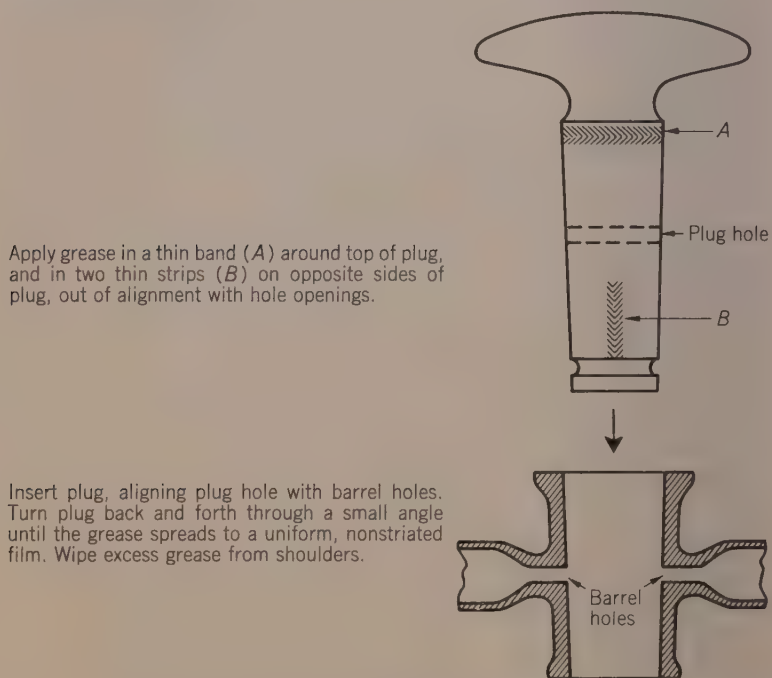


FIG 15.3. How to Grease and Seat a Stopcock

15B.2. Teflon Stopcocks

Teflon-valved equipment is coming into wide use. Teflon stopcocks are much easier to use and maintain than glass stopcocks, since lubricating greases are not required. Teflon stopcocks are very inert and are particularly useful for alkaline solutions, organic solvents, and concentrated acids, which emulsify, dissolve, or attack stopcock greases.

However, certain precautions must be observed with Teflon. It is soft and flows under pressure. Threaded Teflon parts should never be

screwed up tightly, or the threads will become stripped. In storage, it is well to loosen threaded Teflon parts, so that the threads will not become distorted.

Figure 15.4 is a schematic of one type of Teflon stopcock. The nut holds the plug in the barrel. The lock washer turns with the plug and

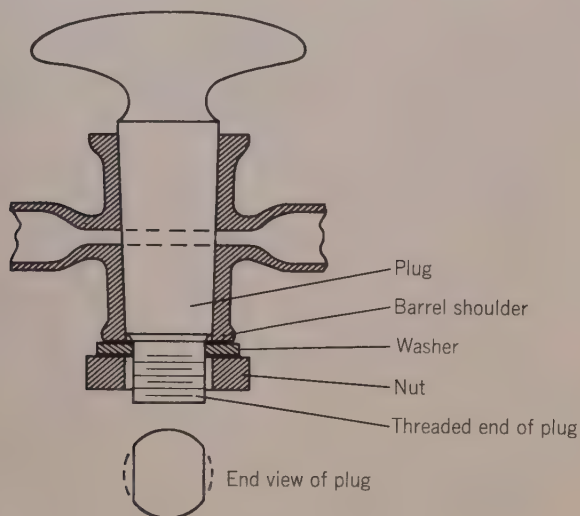


FIG. 15.4. A Teflon Stopcock

slips over the port shoulder. There is no slippage between the nut and the washer, and the nut has no tendency to loosen when the plug is turned. Without the lock washer, the nut would bind on the barrel shoulder and would eventually loosen. Although not necessary, a very thin film of grease applied to the Teflon plug makes for easier operation and reduces chances for leakage.

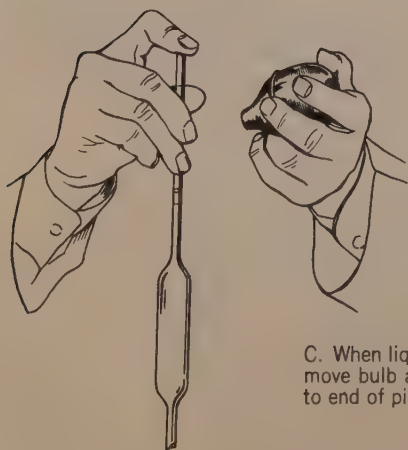
15B.3. Use of the Rubber Bulb

Solutions are most conveniently drawn into pipets by suction. Except in safe and infrequent instances, suction should not be provided by the mouth. The use of a rubber bulb to provide suction is more inconvenient at first than the use of the mouth, but it is much safer, cleaner, and perfectly easy after some practice. A method of using the rubber bulb in pipetting is shown in Fig. 15.5. If the bulb does not have sufficient capacity to fill the pipet completely, the bulb should be momentarily removed when the liquid level stops rising, recompressed, and quickly replaced against the end of the pipet. Under no circumstances should solution ever be drawn into the bulb; if this is done inadvertently



A. Dip pipet tip into liquid to be taken up. Compress rubber bulb in left hand, and hold mouth of bulb firmly against end of pipet. Do not slip bulb over end of pipet.

B. Release compression and liquid will be drawn up slowly. If suction ceases before pipet is full, remove bulb momentarily, recompress, and re-apply.



C. When liquid rises above calibration mark, remove bulb and apply index finger of right hand to end of pipet.

FIG. 15.5. How to Use a Rubber Bulb for Pipetting

the solution should be rejected, and the bulb rinsed with distilled water and allowed to dry before being used again. The rubber bulb is suitable for applying suction (or pressure) to equipment of small volume; for large equipment an aspirator (or air pressure) may be used.

15B.4. Reading the Position of the Meniscus

To make a volumetric measurement, it is necessary to locate the position of the meniscus (i.e., the surface of the liquid) with respect to the markings on the apparatus. The liquid surface is concave, and for

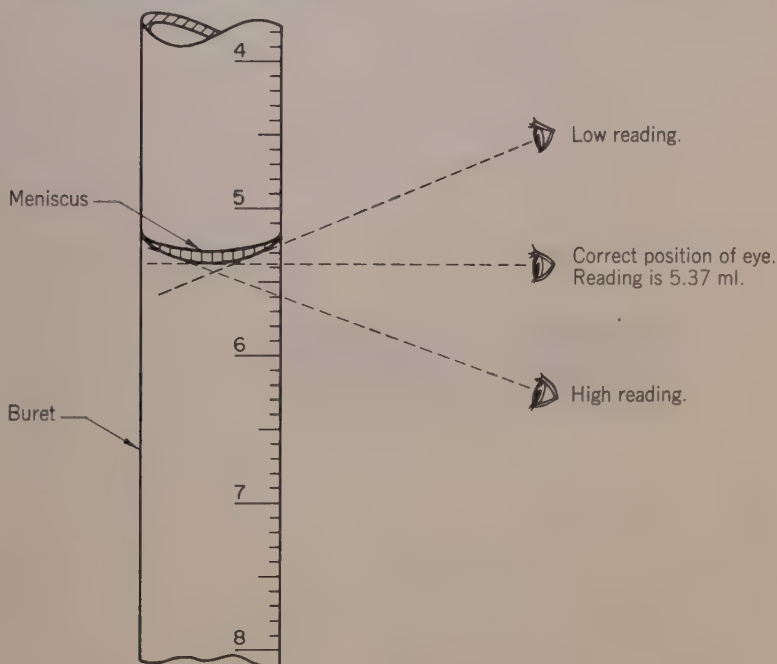
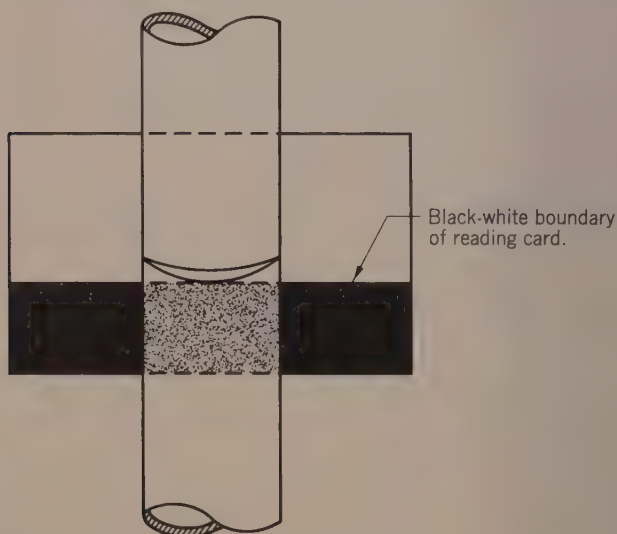


FIG. 15.6. Reading Error Due to Parallax

clear liquids the bottom is most easily located. In narrow tubes, as in the stem of a pipet, the bottom of the meniscus may be precisely located regardless of lighting conditions, and error due to parallax (see below) is negligible.

In burets or flasks, where the diameter of the tube is appreciable, the apparent reading is considerably affected by the position of the eye (see Fig. 15.6). This variation of the apparent position of the meniscus is called *parallax*. Errors due to parallax may be made insignificant with proper technique. The calibration mark on a flask

completely encircle the neck, and the eye should be brought to the level that makes the circle appear as a straight line before the position of the meniscus is read or adjusted. Similarly, the integral milliliter graduations on a buret completely encircle the tube, and it is easy to bring the eye to the proper level by sighting across the full circle nearest to the meniscus. In reading, the eye should be kept at a good distance (12–18 inches) from the mark. The apparent thickness of the meniscus (which is a reflecting lens) depends on the lighting and background, and a reading card (Fig. 15.7) is desirable for reproducibility of the background. The reading card is made by pasting a strip of dull black paper across a 3- by 5-inch filing card.



Reading card correctly held. Meniscus boundary sharp and tangent to black-white boundary. Thickness and location of meniscus are altered when reading card is held incorrectly.

FIG. 15.7. How to Use a Reading Card

Since the graduation marks themselves have a finite thickness (about 0.02 ml on a buret), it is desirable to adopt a fixed convention for reading. The Bureau of Standards recommends reading to the middle of the mark. Some workers find it easiest to read consistently to the top of the mark.

The bottom of the meniscus of a dark or deeply colored solution (as standard KMnO_4 or iodine in KI) may not always be visible and locatable by the procedure above. In such a case the worker should adopt whatever procedure he finds most convenient and precise, such as reading to the top of the meniscus.

15B.5. Measurement of Volumes

There are many correct methods of using volumetric equipment, and a particular worker's technique is largely a personal matter. To achieve good precision, however, fixed and reproducible techniques are essential. It is especially necessary that the technique used in calibration should also be used in measurement. The procedures outlined below are merely suggestions, and the individual student may find it desirable to modify them. Additional volumetric techniques are described in the Supplement (p. 748).

15B.5a. Use of the volumetric flask. The following procedure may be used in diluting to volume in a volumetric flask.

1. The solution to be diluted or the solid to be dissolved is transferred quantitatively to the flask. The transfer is made with a funnel having a stem long enough to reach well into the neck, so that no solute will be retained on the lip or ground-glass area near the very top of the flask. A solid may be transferred in the wet way (p. 112), or, alternatively, it may be placed in the funnel and flushed into the flask with water. By careful swirling, and without removing the funnel, all solids should be dissolved before the flask is three-fourths full. Water is then added through the funnel in such a way as to rinse down its inside, and also along the outside of the stem, until the flask contents reach to the bottom of the neck. The funnel is laid aside, and the flask contents are mixed by careful swirling.

During all of the preceding, it is desirable to handle the flask by the neck, so that the contents will not be unduly warmed by the hands.

2. A thermometer is immersed in the flask and the temperature is taken. The thermometer is then withdrawn, while washing it with a stream of water. More water is added, as necessary, to bring the level to within a millimeter of the mark, the water being added so as to rinse the sides of the flask above the mark. If the ground-glass surface or any bulge in the neck below the lip has become wet, blot off the excess water with a strip of ordinary filter paper wrapped around the end of a stirring rod. Permit the sides to drain for about a minute, and then add water to the mark with a long-tipped dropper, being careful not to get any drops on the flask above the mark.

3. After adjusting to the mark, the flask is stoppered and the contents are thoroughly mixed. The very shape of a volumetric flask prohibits good mixing, and special care is needed to overcome this disadvantage. To mix, the flask is inverted with one hand; the other hand is used to keep the stopper seated. While in the inverted position the flask is shaken briskly with a horizontal motion, and is then set upright. The inversion and the shaking are repeated about ten times. After mixing,

the liquid level may stand above the mark, if the contents have been heated by the hands, but this is of no consequence.

15B.5b. Use of the pipet. The solution is sucked up until it stands above the calibration mark.* Suction is then stopped, and the moistened (not wet) index finger is quickly placed over the end of the pipet before the solution level drops below the calibration mark. The proper method of holding the pipet is shown in Fig. 15.8. With a small piece of tissue, the outside tip of the full pipet is then wiped free of adhering droplets, so that they will not fall into the delivery vessel later. To adjust to the mark, the index-finger pressure is momentarily lessened, allowing the meniscus to fall slowly until it is tangent to the mark, whereupon the index-finger pressure is reapplied. The excess solution may be allowed to fall back into the bulk of solution from which it is taken. The pipet tip is then touched to the side of the vessel from which the solution was withdrawn, so that no partly formed droplet adheres to the tip. This process is called "touching off."

To deliver, the pipet tip is slowly† brought over the delivery vessel, and the contents are allowed to drain from a vertical position for the specified length of time. If the drainage time is not specified, one-half minute of drainage after the meniscus has reached the tip is sufficient. After drainage is complete, the pipet is touched off against the walls of the delivery vessel. Any liquid remaining in the tip should never be blown out.

15B.5c. Use of the buret. Performance of a titration. To fill an ordinary buret, the solution is poured into the top through a funnel,

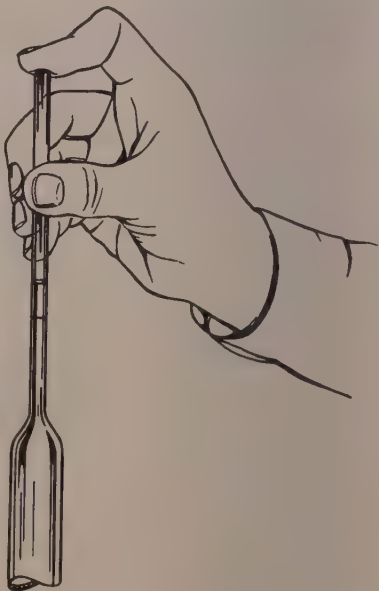


FIG. 15.8. How to Hold a Pipet

*If the pipet is newly cleaned and wet with distilled water, the water must be flushed out with the solution to be measured. This is accomplished by sucking up a small portion of the solution, rolling it around to wet the inner walls, and then rejecting it. This is repeated twice more, so that the liquid remaining in the pipet has virtually the same composition as the solution to be measured. If the pipet is clean and dry, it need not be flushed.

†Sudden motion may cause spurting and loss of liquid.

with special care to prevent overflow as the solution approaches the top. (If wet with distilled water from a previous cleaning, the buret should be rinsed with three consecutive small portions of the solution to be put therein and the portions rejected.) Solution is added until the level stands well over the zero mark, and the funnel is then removed. To flush air from the tip, the stopcock is opened fully for an instant, and then closed again. If any air bells remain, the flushing is repeated. The solution level is then adjusted to the zero mark, and any droplet adhering to the tip is touched off. A minute or so is allowed for drainage, and then the initial reading is made, or the buret is readjusted precisely to the zero mark. (During the waiting period, leaks should be sought by noting if any drops form at the tip, or if the level in the buret drops.)

After the initial reading is made, the titration is begun by running standard solution from the buret into the titration vessel, with constant swirling. As the end point is approached, the rate of addition should be decreased, until finally the titrant should be added only one drop at a time and the titrated solution examined for the indicator change after each drop. When the end point is reached, the specified time interval is allowed to elapse before the final reading is taken. This time interval depends on the method by which the buret is calibrated. For most titrations, 3 minutes is suitable.

There are other useful titration techniques.

1. If the indicator change is a very sharp one, it may be desirable to add standard solution only a half drop at a time near the end point. This may be done by opening the stopcock slightly until a drop begins to form on the buret tip. When the droplet has grown to a few hundredths of a milliliter (one drop is about 0.05 ml), it is touched off to the side of the titration vessel and rinsed down with a little water from the wash bottle. An alternative procedure is to turn the stopcock quickly through the open position, delivering a small spurt of liquid. The volume delivered depends on the rate at which the stopcock is turned. With practice, as little as 0.01 ml may be delivered with none of the liquid adhering to the tip.

2. In general, there is warning as the end point is approached. If the end point is a color change, the change is produced momentarily where the reagent drops into the solution, but fades with stirring into the bulk of solution. This fading occurs more slowly as the end point is approached.

3. If an end point is not sharp, or if it is unfamiliar, it may be difficult to decide when the end point has actually been reached. In this case, it is well to record the buret reading, add another drop, and note the change produced. If the observer is still uncertain, another reading should be recorded, and another drop added. When a series of such

readings have been recorded it is easier to select the end point in retrospect than by direct approach.' The end point is often taken as the volume before that drop that produces the greatest change in the indicator.

4. For each titration in a series, the buret should be refilled to the zero mark.

5. It is extremely important to apply slight pressure when turning the stopcock, to keep it seated. If this is not done, the plug may become unseated and the solution may be spilled. The proper way to turn a stopcock is shown in Fig. 15.9.*

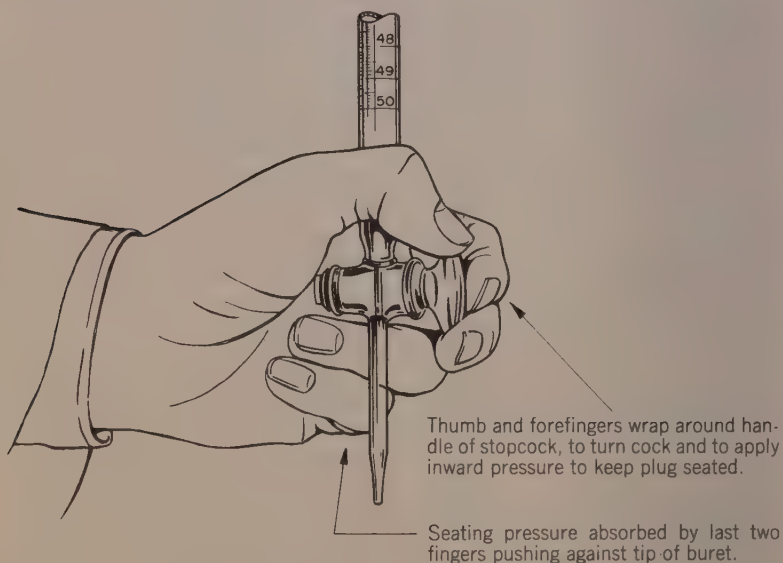


FIG. 15.9. How to Turn a Stopcock

6. There is always the potential danger that an end point will be overrun. This danger is particularly great in the first of a series of titrations, and many such determinations are spoiled irrevocably, with considerable loss of effort. There are several ways to remedy or to guard against this error. (a) Approach the end point slowly. Although this is a good technique if the end point is approximately known beforehand, it may be frustratingly slow on a first titration. (b) Use a second buret, containing a second standard solution of a substance (often the

*Some workers prefer to hold the hand at a downward angle, and to absorb the seating pressure above the stopcock, in the crotch between the thumb and forefinger.

sought-for one) that reacts with the reagent standard solution. When the end point is overrun, the excess reagent may be determined by back titration with the second standard solution. This technique is advantageous where the procedure itself involves a back titration, but not otherwise. Not only is the standard error of reading increased, but there is also the trouble of maintaining and cleaning a second buret. (c) The most desirable procedure is to withdraw about 1% (usually 0.5–1 ml) of the original solution with a dropper. The end point for the rest of the solution is then approached, established, and perhaps deliberately overrun for experience. Then the withheld portion is returned to the titration vessel, the interior of the dropper flushed a few times with the vessel contents, and the final end point (about 1% past the first end point) is carefully approached and established.

7. It sometimes happens that a loosened particle of grease from the stopcock obstructs the buret tip during a titration. Cleaning and re-greasing would not only entail loss of time and effort when such loss can be least afforded, but might also spoil the titration. Two techniques may be used to remove the obstruction without loss of solution. (a) With the stopcock closed, push a fine wire up into the buret tip, making an opening sufficiently large to allow passage of the solution when the stopcock is again opened. (b) With the stopcock closed, apply heat locally and gently to the tip, to soften the obstructing grease so that it may be forced out by hydrostatic pressure when the stopcock is opened. The displacement is often aided by applying pressure to the upper end of the buret with the rubber bulb. Heat should be applied with a very small flame, such as that of a match, so that the stopcock and buret contents do not become heated. Method *b* is more effective than method *a*, but it cannot be used for solutions unstable to heat or flame gases.

15C. ERRORS IN MEASURING VOLUMES

The measurement of volumes at the 0.1% error level is beset with many sources of error, but most of these may be controlled by proper technique. In the following classification, the random errors are ones for which simple corrections cannot be applied, and which must be kept to a minimum by proper experimental techniques; the two determinate errors are allowed to occur and then they are simply corrected for.

For measurement at the 1% error level, only the larger random errors need be guarded against, and calibration and temperature corrections are unnecessary.

15C.1. Random Errors

Variation in properties of the solution. In delivering from burets or pipets, it is tacitly assumed that the properties of the solution that affect the drainage film (density, viscosity, and surface tension) are the same as those of the pure water used to calibrate the apparatus. If this is not the case, the proportion of liquid retained in use is different from that in calibration, and error results. Actually, this error is negligible for dilute (less than 1 *M*) aqueous solutions of most solutes; calibration of apparatus for delivery of such solutions may properly be made with pure water. Where the properties of the solution used are appreciably different from those of pure water, the apparatus should be (1) calibrated with the solution to be used, or (2) used to measure only volumes contained and not delivered.

Nonadditivity of volumes. When two solutions of different compositions are mixed, the resultant volume is seldom the sum of the two original volumes. Thus when 1.000 l of water is mixed with 1.000 l of conc. H_2SO_4 at 20°C, the resultant volume is 1.870 l; the contraction is 0.130 l, or 6.5%. Some other systems undergo expansion. Hence, if it is desired to dilute a solution to one-tenth of its original concentration, it does not suffice to mix 10.00 ml of that solution with 90.00 ml of water and to assume that the final volume is 100.00 ml. This error is avoided by the technique of *diluting to volume*. To dilute a solution tenfold, 10.00 ml of the solution are placed in a 100.00-ml volumetric flask, and an indeterminate amount of water is added to give a precisely known final volume of 100.00 ml.

Personal errors. Personal errors are those for which the worker is directly responsible. They are due largely to carelessness and forgetfulness. Among the errors most frequently encountered in using volumetric equipment are the following: (1) Different techniques in calibration and use. There is enough leeway, however, so that reasonable departures from the conditions of calibration entail only small errors; errors greater than a few tenths of a per cent occur only for flagrant departures. (2) Dirty equipment. Nonreproducible drainage due to contaminated walls may easily cause errors of several tenths of a per cent. Clean apparatus is essential. (3) Trapped air. In filling, air bubbles may be trapped and may adhere to the walls. This can be avoided by filling smoothly, so that the entering solution runs down the walls, rather than plunging into the bulk of solution already in the apparatus. Also, if a buret tip contains air at the initial reading, this bubble causes error if lost in delivery before the final reading is taken. (4) Poor rinsing. Failure to rinse a wet piece of equipment with the solution to be put therein causes indeterminate dilution of that solution. (5) Poor

precision on aliquots of the same solution is sometimes due to poor mixing. (6) Misreading of a buret. This is a rather frequent error. It is quite easy to mistake a half-milliliter mark for a full-milliliter mark, which gives an error of 0.5 ml, or to miscount the unnumbered 0.1-ml divisions. Errors of parallax are not important if proper reading techniques are used. (7) Leaky stopcock. If the grease is old or the seating poor, the stopcock may leak. If the leakage is through the stopcock and into the titration vessel, no error results. If the leakage is between the plug and the barrel of the stopcock, standard solution is lost and error results. Little effort is required to check the buret for leaks, and this should be done frequently. (8) Computational error. Computations are a frequent cause of error. In titrating only an aliquot portion of a sample, a particularly common error is failure to multiply the result by the aliquot factor.

15C.2. Determinate Errors

15C.2a. Incorrect capacity. The true volume of a piece of equipment is not always the nominal volume. For precise work, each piece of equipment should be calibrated—that is, the volume should be accurately determined. This is particularly true if the history is unknown, or if the apparatus has been repaired or altered in any way.

The most frequently used procedure for calibration is a gravimetric one. Here the weight of water contained or delivered is measured with the balance; from the known density of water, the volume contained or delivered is calculated. The advantage of this procedure lies in its accuracy; gravimetric measurements are far more accurate than volumetric. The principal disadvantage lies in the time required. Other calibration methods are discussed in the Supplement (p. 751).

In computing the volume of water contained or delivered from its density and its weight in air against brass weights, both temperature and buoyancy corrections must be made. Although the computations are not difficult, they are time consuming, especially since many are required to calibrate a whole set of volumetric equipment. To facilitate computations, Table 15.1 may be used. The title of this table is self-explanatory, and the following examples should clarify its use. Derivation of the volumes in Table 15.1 is described in the Supplement (p. 751).

In reporting the result of a calibration, only the calibration correction is usually given, and not the true volume. The calibration correction is defined as that quantity (in milliliters) that must be added to the nominal volume to give the true volume.

$$\text{True volume} = \text{nominal volume} + \text{calibration correction} \quad (15.1)$$

Example 1. What is the calibration correction of a 10-ml pipet that delivers 9.93 g of water at 19°C, weighed in air against brass weights?

$$\text{Pipet volume} = 9.93 (1.0026) = 9.96 \text{ ml (at } 20^{\circ}\text{C)}$$

$$\text{Calibration correction} = 9.96 - 10 = -0.04 \text{ ml (at } 20^{\circ}\text{C)}$$

Example 2. What weight of water, weighed in air against brass weights, would have to be put into a flask at 27°C, so that the flask may be marked to contain 1.0000 l at 20°C?

At 27°C, one gram of water is contained in a glass flask whose volume at 20°C is 1.0043 ml.

A glass flask whose volume at 20°C is 1.0000 ml would therefore contain 1.0000/1.0043 g of water at 27°C.

A glass flask whose volume at 20°C is 1000.0 ml would therefore contain $1000.0(1.0000/1.0043) = 995.7 \text{ g H}_2\text{O}$ at 27°C. Short-cut methods of computation are described in the Supplement (p. 643).

TABLE 15.1

THE VOLUME OF A GLASS CONTAINER (CORRECTED* TO 20°C) THAT CONTAINS ONE GRAM† OF WATER AT VARIOUS TEMPERATURES

Temperature (°C)	Volume (ml)	Temperature (°C)	Volume (ml)
10.....	1.0016	23.....	1.0034
11.....	17	24.....	36
12.....	18	25.....	38
13.....	19	26.....	41
14.....	20	27.....	43
15.....	21	28.....	46
16.....	22	29.....	48
17.....	23	30.....	51
18.....	25	31.....	54
19.....	26	32.....	56
20.....	28	33.....	59
21.....	30	34.....	62
22.....	32	35.....	66

*The container volumes could be given at each temperature, but for uniformity, a standard temperature of 20°C has been adopted (see Supplement, p. 751).

†Weighed in air with brass weights.

15C.2b. Temperature variations. It is conventional to express volumes of all glassware at 20°C, as is done in Table 15.1. If used at a temperature different from 20°C, the volume of glassware is of course different from that computed according to Table 15.1. However, owing to the small expansion coefficient of glass (0.0025% per °C), the difference is negligible for all ordinary analytical work within the range of 10–35°C.

Example 1. A flask is found by calibration to contain 100.09 ml at 20°C. What is the volume of this flask if used at 29°C?

Expansion of glass from 20° to 29°C is $9(0.0025) = 0.023\%$, which is negligible when working at the 0.1% error level.

In terms of milliliters, the expansion is $(100.09)(0.00023) = 0.023$ ml, making the volume of the flask 100.11 ml.

The effect of temperature on the concentration of solutions, however, is appreciable. If the temperature increases, the volume of solution expands, but the amount of solute remains unchanged; hence the concentration decreases. For precise work, whenever a concentration is given, the temperature at which that concentration was measured should also be given. For temperature changes in the range of 15–35°C, and for dilute solutions (0.1 *M* or less), concentration changes may be computed with sufficient accuracy for ordinary work by assuming an expansion coefficient of 0.02% per °C. For more precise work, the specific volumes in Table 15.1 must be used.

Example 2. What is the concentration at 20°C of a solution that is 0.0962 *N* at 30°C?

Method A. The concentration at 20°C is greater than it is at 30°C by $10 \times 0.02 = 0.2\%$. The concentration increase is therefore $0.002 \times 0.0962 = 0.00018$ *N*, and the concentration at 20°C is $0.0962 + 0.00018 = 0.0964$ *N*.

Method B. From Table 15.1, the ratio of the volumes of the same weight of solution at 30°C to that at 20°C is 1.0051/1.0028. Therefore, the concentration at 20°C is $0.0962 \times 1.0051/1.0028 = 0.0964$ *N*.

15C.2c. Typical titration data. From the foregoing sources of error, it is apparent that a titration involves more than simply the taking of initial and final volume readings on a buret. For example, the data used to find the normality of an acid solution by titrating at 30°C with a standard base solution having a concentration of 0.1035 *N* at 20°C might look like this:

Volume of Acid Used	Volume of Base Used (0.1035 <i>N</i> at 20°C)
	0.00 initial reading
	22.81 final reading
25.00 nominal volume of pipet	22.81 (uncorrected)
–0.03 calibration correction	+0.02 (calibration correction)
<hr/> 24.97 ml (30°C)	<hr/> 22.83 (30°C)

In computing the concentration of the acid, either the concentration of the base at 30°C could be computed and used with the volumes measured at 30°C, or the volumes could be corrected to 20°C for use with the normality of the base as given at 20°C. When many titra-

tions with different standard solutions are performed over a period of time, it is desirable to reduce all volumes and concentrations to a standard temperature, such as 20°C. If the laboratory temperature varies over a range of less than 5°C, temperature corrections may be dispensed with at the 0.1% error level.

15D. CALIBRATION EXPERIMENTS

The excellence of volumetric apparatus today leaves little to be desired, for such apparatus is almost always correct within very narrow tolerance limits. If this is so, the question arises as to whether the student should take his valuable time to check such apparatus. The answer is that he should, for the very excellence of his equipment furnishes a check upon his technique. If a student's calibration does not check within required tolerances, the first source of error should be sought in technique, rather than in the apparatus.

For all experiments in this text, only the 50-ml pipet, the 250-ml and the 500-ml flasks, and the two 50-ml burets need be calibrated. These calibrations should be completed before any volumetric determinations are undertaken. It is suggested that the calibration corrections for all pieces of equipment be entered upon a single accessible page in the notebook, since constant reference must be made to these data for subsequent experiments. All calibrated equipment should be well identified and set apart, to avoid unnecessary use and mix-up with other equipment.

To calibrate all volumetric equipment precisely is time consuming. By putting justifiable confidence in the quality of modern equipment, the time may be shortened, because the only purpose of calibration is to check the student's technique. The following modifications are suggested, to be designated by the instructor: (1) Omit calibration of the flasks, which are almost always within a few hundredths of a per cent of the nominal volume. (2) Do calibrations only once (not in duplicate), but repeat those that fall outside tolerances. (3) Calibrate only one buret. (4) Perform only a two-point calibration on the buret—at 30 and 45 ml.

EXPERIMENT 15.1. CALIBRATION OF THE 50-ML PIPET

PROCEDURE

1. Clean the pipet, but do not bother to dry it.
2. Weigh the 125-ml Erlenmeyer flask with a rubber stopper to the nearest few milligrams. (Notes 1, 2.)

3. Fill the pipet with distilled water from a beaker of water containing a thermometer, so that the temperature of the water is known.

4. Deliver the contents of the pipet into the weighed flask, and weigh again. (Note 3.)

5. Find by difference the weight of water delivered, and then find the volume of the pipet, using Table 15.1. Calculate the calibration correction. (Note 4.)

6. Repeat the calibration of the pipet. (Note 5.) The average of the two determinations should be used as the calibration correction for the pipet in all future work.

NOTES

(1) Since the precision striven for is of the order of 0.01 ml, weighings need be made only to about 10 mg. It is sufficient merely to counterbalance the load with weights until the pointer remains on the scale when the balance is released. Weighings may be made very rapidly in this way.

(2) Prepare two stoppered flasks, and use the lighter combination as a tare (p. 82).

(3) Unless otherwise specified, a drainage time of a half-minute after the meniscus reaches the pipet tip is recommended.

(4) The calibration correction will usually fall within the range of ± 0.05 ml.

(5) Duplicate determinations should agree within 0.03 ml.

EXPERIMENT 15.2. CALIBRATION OF THE VOLUMETRIC FLASK

PROCEDURE

1. Clean the 500-ml flask, and allow it to dry.

2. Weigh the dry, empty flask by substitution upon the oversized balance. (Note 1.)

3. Fill the flask to the mark with water whose temperature is known, and weigh again by substitution.

4. Find the weight of water contained, and from this weight find the volume and calibration correction of the 500-ml flask, using Table 15.1. (Note 2.)

5. Repeat the calibration of the 500-ml flask. (Note 3.)

6. Perform duplicate calibrations of the 250-ml flask in the same manner. (Note 4.)

NOTES

(1) Because the ratio of the lengths of the balance arms may be considerably different from unity, the method of substitution should be used in weighing. In weighing by substitution, a tare is required. Lead shot serves well for the tare. A beaker should be used to hold the shot, which should not be placed directly in the pan.

(2) The calibration correction will usually fall within the range of ± 0.15 ml.

(3) Duplicate determinations should agree within 0.08 ml.

(4) Duplicate determinations should agree within 0.05 ml, and the average calibration correction will usually fall within the range of ± 0.11 ml.

EXPERIMENT 15.3. CALIBRATION OF THE 50-ML BURET

PROCEDURE

1. Weigh the 125-ml Erlenmeyer flask with a rubber stopper to the nearest few milligrams. (Note 1. Also see Note 2, Exp. 15.1.)

2. Fill the clean buret with distilled water, and adjust to the zero mark. (Notes 2, 3.)

3. Deliver a 20.00-ml portion (Note 3) into the weighed flask.

4. Weigh the flask plus water. Calculate the volume from the weight of water delivered, using Table 15.1. Calculate the calibration correction for the 0–20-ml interval. (Note 4.)

5. Repeat the calibration for the 0–20-ml interval. (Note 5.)

6. Perform duplicate calibrations on the intervals 0–30, 0–40, and 0–50 ml. (Note 5.)

7. Plot the average calibration corrections (in hundredths of a milliliter, as ordinates) against buret readings (in milliliters, as abscissae) for each of the four intervals measured. Draw a broken-line curve through the points.

NOTES

(1) If two burets are calibrated, it is suggested that they be calibrated in parallel, with a consequent saving in time and effort.

(2) To adjust precisely to a certain mark, run within about 0.1 ml short of that mark, wait until a few seconds before the end of the drainage time, adjust to the desired reading, touch off the pendant drop, and read.

TABLE 15.2
DATA AND COMPUTATION SHEET FOR BURET CALIBRATION

BURET No.								
BURET READING (ML)		TEMPERATURE (°C)	WEIGHT OF FLASK (g)		WEIGHT OF WATER DELIVERED (g)	VOLUME DELIVERED (ML)		CALIBRATION CORRECTION (ML)
Initial (1)	Final (2)		Empty (4)	Full (5)		Apparent (7) (2 – 1)	Calculated (8)	
		(3)	(4)	(5)	(6) (5 – 4)	(7)	(8)	(9) (8 – 7)
0.01	20.02	23	27.123	47.086	19.963	20.01	20.03	0.02

(3) If the mark is overrun, it is not necessary to repeat the delivery. The initial and final readings may fall anywhere about 0 and 20 ml, respectively, so long as they are precisely measured.

- (4) A suggested tabular form for the data and calculations is given in Table 15.2.
- (5) Calibration corrections will usually fall within about 0.1% of the apparent volume. On any interval, duplicate calibrations should agree within 0.03 ml.

EXPERIMENT 15.4. RELATIVE CALIBRATION OF THE 250-ML FLASK AND THE 50-ML PIPET

If many analyses are performed in which aliquots of a single sample are titrated, it is desirable to calibrate the volumetric flask and pipet relative to each other, so that when an aliquot pipetful is taken it will amount to a simple, integral fraction of the sample, thus simplifying computations. The calibration procedure is as follows:

1. Using standard technique, deliver five 50-ml pipetfuls of distilled water into the clean, dry, 250-ml flask. Mark the liquid level with a gummed label. Empty the flask, clean and dry it, and repeat the calibration.

2. In use, when a sample is placed in the flask and diluted to the mark above, an aliquot withdrawn and delivered with the 50-ml pipet is precisely a one-fifth aliquot. This mark holds only for the particular pipet used in calibration.

QUESTIONS

Section 15A

1. Explain the operation of an automatic zero buret with a two-way stopcock.
2. Explain why the transfer pipet is a more precise instrument than a measuring pipet of the same volume.

Section 15B

1. Describe the performance of each of the following operations, giving reasons for each step in each operation. (a) Measure out precisely a volume of standard solution around 25 ml. (b) Measure out precisely 28.23 ml of a standard solution. (c) Prepare about a liter of a 0.1000 *M* solution of a primary standard substance. (d) Dilute a 27.65-ml portion of standard solution precisely tenfold, within an error of 0.1%.
2. Considering that the size of a drop falling from a buret tip is about 0.05 ml, are the techniques of "touching off" and "splitting" drops spurious in ordinary volumetric analysis?
3. Why should a buret always be refilled to the zero mark each time a portion is withdrawn?
4. Describe the technique of reading a mercury meniscus.
5. Devise methods of avoiding error due to parallax other than that described in the text.

Section 15C

1. What is the meaning of a negative calibration correction?
2. Devise and outline procedures for performing the following tasks, giving directions for any computations involved. (a) Calibrate a volumetric flask to contain

1000.0 ml. (b) Calibrate a volumetric flask to deliver, using the mark that is already on the flask. How does the volume contained compare with that delivered? Give precautions in using a flask to deliver. (c) Deliver precisely 567.2 ml of a standard solution into a clean, dry container, with no dilution. An excess of solution and ordinary student equipment are available. (d) Measure out precisely 998.1 ml of a standard solution. (e) Quickly calibrate a 50-ml volumetric flask, using a calibrated 50-ml pipet. (f) Quickly calibrate a volumetric flask to contain 1000.0 ml, knowing that the calibration mark is at 1001.5 ml, and using a 5-ml measuring pipet. (g) Prepare a 0.1000 *N* solution of HCl, starting with conc. HCl. (h) Within an error of 0.1%, measure out 10 mg of a stable, water-soluble primary standard substance, using only an ordinary balance and volumetric equipment.

3. In making up a solution from an expensive primary standard in a 250-ml volumetric flask, the flask is inadvertently filled to several millimeters above the mark. Tell how you would "save" the solution, with as little effort as possible, and still know the concentration within 0.1%.

4. Why are temperature variations considered a source of determinate error in volumetric analysis?

5. A pipet is calibrated to deliver 10.00 ml of water. What would be the direction of the error if this pipet were used to deliver (a) conc. H_2SO_4 , (b) acetone, (c) mercury?

6. A worker weighs out a sample, dissolves it, and dilutes it to 250.0 ml, with the intention of performing replicate titrations on 50-ml aliquots. After titrating the first aliquot, he finds that the solution was incompletely mixed. Can the worker properly mix the remaining solution and proceed with the analysis? Explain.

7. A worker has a standard 0.1 *N* base solution, and he wishes to determine the H_2SO_4 content of a bottle of conc. H_2SO_4 . Without discussion, outline the steps that he would perform in obtaining the solution that he titrates.

Section 15D

1. In calibrating a 3-l volumetric flask, with water, how accurately should weighings be made for work at the 0.1% error level?

2. What would be the direction of the error if a properly calibrated pipet were used to deliver at an angle of about 45° ?

3. On calibration by a student, a 50-ml pipet was found to deliver 50.15 ml. Explain what should be done.

4. A flask and pipet are calibrated relative to each other. How does the calibration depend on temperature?

5. Draw an approximate calibration curve for a buret that has a perfectly linear scale of markings, has a perfectly uniform bore, and that delivers: (a) 50.00 ml for the interval 0–50 ml. (b) 50.10 ml for the interval 0–50 ml. (c) 30.10 ml for the interval 0–30 ml. (d) 29.90 ml for the interval 0–30 ml.

6. Repeat Ques. 5, if in addition the buret has a 0.05-ml outward bulge between 40 and 41 ml.

7. Draw an approximate calibration curve for a buret that has a perfectly linear scale of markings, has a bore that tapers uniformly, being smaller at the bottom than the top, and that delivers: (a) 50.00 ml for the interval 0–50 ml. (b) 50.10 ml for the interval 0–50. (c) 30.10 ml for the interval 0–30. (d) 29.90 ml for the interval 0–30 ml.

8. Repeat Ques. 7, if in addition the buret has a 0.05-ml outward bulge between 40 and 41 ml.

9. Draw a graph showing approximately how the error would depend on the angle at which a pipet is held during delivery.

PROBLEMS

Section 15A

1. The inside diameter of the stem of a 10-ml pipet is 3 mm. If the error in adjusting the meniscus is 0.2 mm, what is the corresponding error of the volume? Considering that the error of delivery is about 0.01 ml, is adjustment of the meniscus a predominant source of error? What is probably the predominant source of error?

Ans. 0.001 ml; no; drainage.

2. Assume that a micropipet contains a volume of 0.05 ml. What should be the inside diameter of its stem so that an error of 0.2 mm in adjusting the meniscus may give an error of only 0.1% in the volume?

3. The inside diameters at the markings of 25-ml transfer and measuring pipets are 3 mm and 9 mm, respectively. For a given error (say, 0.2 mm) in adjusting the meniscus, what is the ratio of the errors in volume delivered from the two kinds of pipets? Assume no other sources of error.

Ans. 1:9.

Section 15C

1. What is the calibration correction of a 50-ml pipet that delivers 49.82 g of water at 26°C?

Ans. 0.02 ml.

2. What is the calibration correction of a buret that delivers, in replicate determinations from 0.00 to 30.00 ml, the following weights of water at 29°C: 29.92, 29.95, 29.96, 29.93 g? What is the range (a) in milliliters, (b) in per cent?

3. What is the percentage error of using without correction a solution at 29°C that is standardized as 0.1596 *N* at 18°C?

Ans. -0.23%.

4. A 0.1800-mole portion of AgNO_3 is dissolved and made up to volume at 26°C in a flask having a volume of 999.82 ml. What is the molarity of the solution at 26°C? At 20°C?

5. A solution is measured as 0.1560 *N* at 20°C. What is the normality at 28°C?

Ans. 0.1557 *N*.

6. The concentration of an AgNO_3 solution is 0.1000 *M* (18°C), and that of an NaCl solution is 0.1000 *M* (30°C). What volume of AgNO_3 is required to react with 25.00 ml of the NaCl , both solutions being measured out at 24°C?

7. An NaCl solution is measured as 0.1156 *M* at 16°C. What volume, measured at 29°C, should be taken to give 4.000 mmoles of NaCl ?

Ans. 34.69 ml.

8. What is the volume at 35°C of a 500-ml flask that has a volume of 500.0 ml at 20°C?

9. A liter flask is calibrated to the mark and found to contain a volume of 999.4 ml at 20°C. If the diameter of the neck is 15 mm, how far above the mark must a second mark be placed to denote 1000.0 ml?

Ans. 3.4 mm.

10. The inside diameter of the neck of a 1-l volumetric flask is 15 mm. A standard solution is properly made up in this flask by adjusting to the mark at 26°C. In mixing, heat from the hands warms the contents to 27°C. How high above the mark does the meniscus stand?

11. The concentration of an acid solution (about 6 *N*) is to be determined precisely by titration with 0.0875 *N* base. How should the acid solution be diluted with student apparatus, so that a 50-ml aliquot of the diluted solution will require 25–50 ml of the standard base for titration?

Ans. 10-ml pipetful in a 1-l flask.

12. A base solution is 0.1216 *N*. Explain how to obtain 0.1000 *N* solution from it, outlining any necessary calculations.

13. In determining the capacity of a 500-ml flask, what error is allowable in measuring the temperature, if the allowable error in volume is 0.2 ml?

Ans. 2°C.

14. In the calibration of a buret at 26°C, the following data were obtained. Draw the calibration curve.

BURET READINGS (ML)		GRAMS OF WATER DELIVERED
Initial	Final	
0.01	20.03	19.91
0.12	30.00	29.75
0.01	40.03	39.85
0.02	49.80	49.60

15. From the data on page 265, calculate the acid normality in the ways suggested.

Ans. 0.0946 *N* (20°C); 0.0944 *N* (30°C).

16 TITRATIONS BASED ON PRECIPITATION REACTIONS

Volumetric precipitation processes are discussed generally in this chapter. However, almost all illustrations are argentimetric—that is, illustrations in which Ag is the standard or sought-for substance. Argentimetric methods are selected because (1) they are frequently used and are well established; (2) they are precise, simple, and suitable for student use; and (3) they illustrate almost all the important principles, methods, and limitations of volumetric precipitation reactions.

16A. TITRATION CURVES

16A.1. Description and Calculation

Suppose that a solution of NaCl is titrated with standard AgNO₃. As soon as the first drop of AgNO₃ is added, AgCl is formed, and some Ag⁺ exists in solution because of the equilibrium



Up to the equivalence point, [Ag⁺] is very small, since NaCl is in excess; but after the equivalence point AgNO₃ is in excess and [Cl⁻] is very small. A plot showing how the concentration of one of the reacting substances (i.e., [Ag⁺] or [Cl⁻]) depends on the volume of added titrant (i.e., standard AgNO₃) is called a *titration curve*. Study of titration curves gives valuable information about the proper performance of titrations. Such curves may be experimentally determined, or they may be calculated approximately, as in the following example. Calcula-

lation of titration curves is useful to the student, because a feeling is obtained for the variables upon which the shape and slope of the curve depend, and upon which the sharpness of the end point depends.

Example. A 50.00-ml portion of 0.1000 *M* NaCl is titrated with standard 0.1000 *M* AgNO₃. Calculate [Cl⁻], [Ag⁺], *p*Cl, and *p*Ag when 10.00 ml of the standard AgNO₃ are added. (Assume that *K_s* for AgCl is 1.0×10^{-10} , and neglect activity and complexing effects.)

Because of the low accuracy of solubility-product calculations when activity effects are ignored, ion concentrations are calculated with uncertainties of 1–10%. Within this range of error, volumes are additive.

After 10.00 ml of 0.1000 *M* AgNO₃ are added to 50.00 ml of 0.1000 *M* NaCl, but before precipitation, the composition of the system is

$$\text{mmoles NaCl} = 0.1000 \times 50.00 = 5.000$$

$$\text{mmoles AgNO}_3 = 0.1000 \times 10.00 = 1.000$$

$$\text{Volume} = 50.00 + 10.00 = 60.00 \text{ ml}$$

The excess chloride concentration is, therefore,

$$\frac{5.000 - 1.000}{60.00} = 0.067 \text{ } M$$

From here, the problem is to calculate [Ag⁺] and [Cl⁻] in a solution saturated with AgCl and containing an excess of 0.067 *M* NaCl.

$$[\text{Ag}^+][\text{Cl}^-] = 1.0 \times 10^{-10}$$

Letting [Ag⁺] = *x*, the chloride concentration becomes 0.067 + *x*. Then

$$(x)(x + 0.067) = 1.0 \times 10^{-10}$$

$$x, \text{ or } [\text{Ag}^+] = 1.5 \times 10^{-9} \text{ } M$$

$$[\text{Cl}^-] = 0.067 + 1.5 \times 10^{-9} \text{ } M, \text{ or approximately } 0.067 \text{ } M$$

$$p\text{Ag} = -\log [\text{Ag}^+] = -\log (1.5 \times 10^{-9}) = 8.82$$

$$p\text{Cl} = -\log [\text{Cl}^-] = -\log 0.067 = 1.18$$

$$(\text{Note that } p\text{Ag} + p\text{Cl} = pK_s.)$$

Ion concentrations may be calculated similarly for other points in the titration, with results shown in Table 16.1. (In the region of the equivalence point, where the excess concentration of NaCl or AgNO₃ is very low, it may be necessary to solve quadratic equations.)

The data of Table 16.1 are plotted in Figs. 16.1 and 16.2. Figure 16.1 contains plots of [Ag⁺] and [Cl⁻] versus volume of standard AgNO₃ added. Although this shows what happens over the course of the whole titration, it does not show clearly what happens in the region of the equivalence point, which is of special interest. Figure 16.2 contains

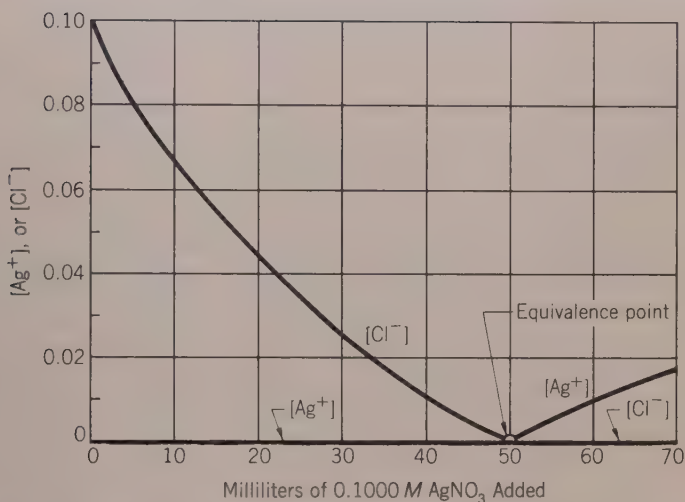


FIG. 16.1. Titration of NaCl with AgNO₃—Conditions: 50.00 ml of 0.1000 M NaCl titrated with 0.1000 M AgNO₃. K_s for AgCl is 1.0×10^{-10} . Activity and complexing effects disregarded. Volumes assumed additive.

plots of pAg and pCl against volume of standard AgNO₃ added, and is the logarithmic counterpart of Fig. 16.1. The logarithmic curves are usually used to describe the course of a titration, for they clearly show how rapidly the ion concentrations change in the region of the equivalence point. Generally, if a quantity varies over a wide range, it is advantageous to express it in log units, rather than directly, and to graph it on a log scale rather than on a linear one.

16A.2. Factors Affecting the Shape of a Titration Curve

Concentration of sought-for substance. Figure 16.3 shows curves for the same titration as Fig. 16.2, but with the NaCl sample initially diluted to give different equivalence-point volumes. It may be seen that (1) the steepest part of the curve is at the equivalence point for all volumes, but (2) the steepness of the curve through the region of the equivalence point decreases as volume increases (i.e., as concentration of sought-for substance decreases). Similar considerations show that the steepness decreases as the concentration of the standard solution decreases.

Solubility of the precipitate. Figure 16.4 shows titration curves for the same type of titration as Fig. 16.2, except that the AgCl type of precipitates formed have different solubility products. It may be seen that (1) the steepest part of the titration curve is at the equivalence

TABLE 16.1

VOLUME AND CONCENTRATION RELATIONSHIPS IN THE TITRATION OF NaCl WITH AgNO₃

Conditions: 50.00 ml of 0.1000 M NaCl titrated with 0.1000 M AgNO₃. K_s for AgCl is 1.0×10^{-10} . Activity and complexing effects disregarded. Volumes assumed additive.

VOLUME AgNO ₃ ADDED (ML)	TOTAL VOL- UME (ML)	EXCESS CONCENTRATION, M		ION CONCENTRATIONS			
		NaCl	AgNO ₃	[Ag ⁺] ($M \times 10^5$)	[Cl ⁻] ($M \times 10^5$)	p_{Ag}	p_{Cl}
0.01	50	0.100	0	0.00010	10,000	9.00	1.00
10.00	60	0.067	0	0.00015	6,700	8.82	1.18
20.00	70	0.043	0	0.00023	4,300	8.64	1.36
30.00	80	0.025	0	0.00040	2,500	8.40	1.60
40.00	90	0.0111	0	0.00090	1,110	8.05	1.95
45.00	95	0.0053	0	0.0019	530	7.72	2.28
47.50	98	0.0025	0	0.0040	250	7.40	2.60
49.00	99	0.00101	0	0.0099	101	7.00	3.00
49.50	100	0.00050	0	0.020	50	6.70	3.30
49.75	100	0.00025	0	0.040	25	6.40	3.60
49.90	100	0.000100	0	0.099	10.1	6.00	4.00
49.95	100	0.000050	0	0.19	5.2	5.72	4.28
50.00	100	0	0	1.00	1.00	5.00	5.00
50.05	100	0	0.000050	5.2	0.19	4.28	5.72
50.10	100	0	0.000100	10.1	0.099	4.00	6.00
50.25	100	0	0.000250	25.0	0.040	3.60	6.40
50.50	100	0	0.00050	50	0.020	3.30	6.70
51.00	101	0	0.00099	99	0.0101	3.00	7.00
52.50	102	0	0.00245	245	0.0041	2.61	7.38
55.00	105	0	0.0048	480	0.0021	2.32	7.68
60.00	110	0	0.0091	910	0.00110	2.04	7.96

point for all values of K_s , but (2) the steepness of the curves through the region of the equivalence point decreases as K_s increases (i.e., as solubility of the precipitate increases). Any factor affecting K_s , therefore affects the shape of the titration curve.

Adsorption. The curves of Figs. 16.2 to 16.4 are calculated on the assumption that only the solubility equilibrium is important in the titrated system. This is not always the case. Adsorption, for example, may cause the experimentally observed titration curve to be substantially different from that calculated from the solubility equilibrium alone, particularly in the region of the equivalence point, where adsorption may reduce the slope of the curve.

Type of precipitate. Titration curves are quite symmetrical in the region of the equivalence point, when the precipitates formed are of the symmetrical type, such as AgCl or BaSO₄. For nonsymmetrical precipitates, such as Ag₂CrO₄, the curve is not symmetrical, and the

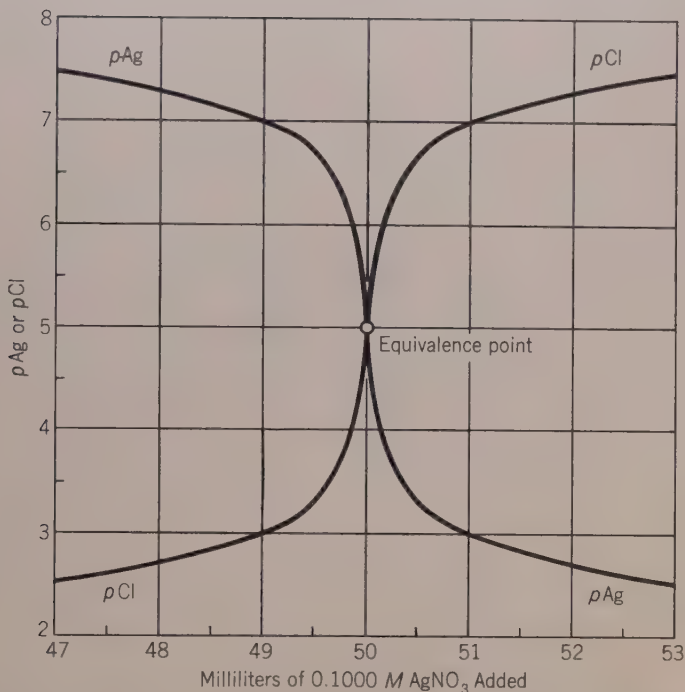


FIG. 16.2. Titration of NaCl with AgNO₃—Conditions: 50.00 ml of 0.1000 *M* NaCl titrated with 0.1000 *M* AgNO₃. K_s for AgCl is 1.0×10^{-10} . Activity and complexing effects disregarded. Volumes assumed additive.

point of steepest slope is not identical with the equivalence point. However, if the precipitate is fairly insoluble, then the curve is steep, and the difference between the point of steepest slope and the equivalence point is negligible. This subject is discussed more fully in the Supplement (p. 754).

Example. A 50.00-ml portion of 0.0600 *M* K₂CrO₄ is titrated with 0.1000 *M* AgNO₃. Calculate *pAg*: (a) at the equivalence point, (b) 1.00 ml before the equivalence point, (c) 1.00 ml after the equivalence point. (d) Compare the rate of change of *pAg* before and after the equivalence point.

(a) At the equivalence point, the required volume of AgNO₃ is

$$\frac{50.00 \times 0.0600 \times 2}{0.1000}, \text{ or } 60.00 \text{ ml}$$

Since the total amounts of Ag⁺ and CrO₄²⁻ are equivalent, and since the precipitated amounts are equivalent, the amounts left in solution are equivalent. There-

fore, if $[\text{Ag}^+] = x \text{ M}$, then $[\text{CrO}_4^{2-}] = x/2 \text{ M}$, and the solubility-product expression gives

$$[\text{Ag}^+]^2[\text{CrO}_4^{2-}] = K_s$$

$$(x)^2(x/2) = 1.29 \times 10^{-12}$$

$$x, \text{ or } [\text{Ag}^+] = 1.37 \times 10^{-4} \text{ M}$$

$$(p\text{Ag})_{\text{eq pt}} = -\log [\text{Ag}^+] = -\log (1.37 \times 10^{-4}) = 3.86$$

(b) When 1.00 ml less than the equivalent volume of AgNO_3 is added,

$$\text{mmoles } \text{K}_2\text{CrO}_4 = 50.00 \times 0.0600 = 3.000$$

$$\text{mmoles } \text{AgNO}_3 = 59.00 \times 0.1000 = 5.900$$

$$\text{Volume} = 50.00 + 59.00 = 109.00 \text{ ml}$$

The concentration of excess CrO_4^{2-} is, therefore,

$$\frac{3.000 - 5.900/2}{109.00}, \text{ or } 4.58 \times 10^{-4} \text{ M}$$

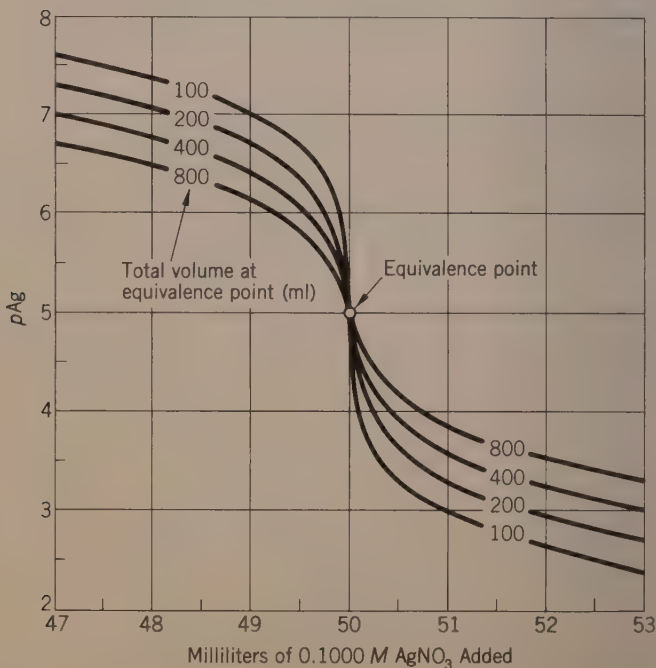


FIG. 16.3. Dependence of Form of Titration Curve upon Concentration—Conditions: 50.00 ml of 0.1000 M NaCl diluted with water, and then titrated with 0.1000 M AgNO_3 . K_s for AgCl is 1.0×10^{-10} . Activity and complexing effects disregarded. Volumes assumed additive.

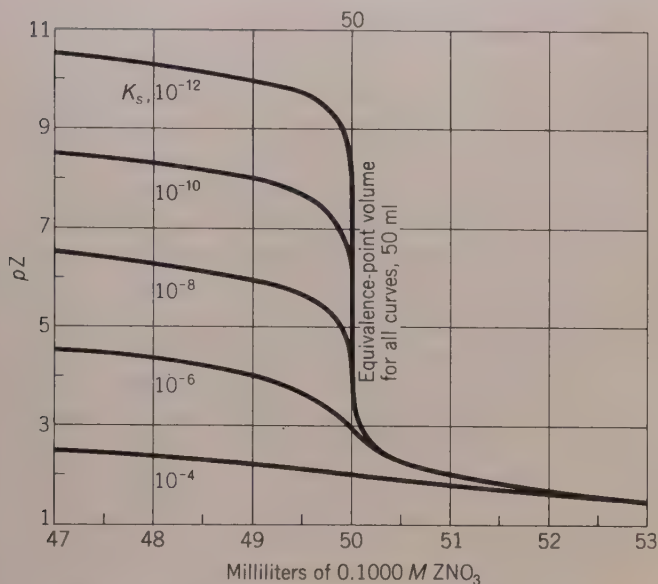


FIG. 16.4. Dependence of Form of Titration Curve upon Solubility Product—Conditions: 50.00 ml of 0.1000 M NaX titrated with 0.1000 M ZNO_3 , to form insoluble ZX , having a solubility product K_s . Activity and complexing effects disregarded. Volumes assumed additive.

From here, $[\text{Ag}^+]$ may be calculated with the aid of the solubility-product expression. Letting $[\text{Ag}^+] = y$ M ,

$$[\text{Ag}^+]^2[\text{CrO}_4^{2-}] = K_s$$

$$(y)^2 \left(\frac{y}{2} + 4.58 \times 10^{-4} \right) = 1.29 \times 10^{-12}$$

$$y, \text{ or } [\text{Ag}^+] = 5.2 \times 10^{-6} \text{ } M$$

$$p\text{Ag} = -\log [\text{Ag}^+] = -\log (5.2 \times 10^{-6}) = 4.28 \text{ (at 59 ml)}$$

(c) When 1.00 ml more than the equivalent volume of AgNO_3 is added, it may be shown that $p\text{Ag}$ is 3.04.

(d) At 59, 60, and 61 ml of AgNO_3 , the $p\text{Ag}$'s are, respectively, 4.28, 3.86, and 3.04. Before the equivalence point, $p\text{Ag}$ changes by 0.42 units per milliliter of AgNO_3 , whereas after, it changes much more rapidly—by 0.82 units per milliliter. These unequal rates of change should be contrasted with the equal ones in the $\text{Ag}^+ \text{--} \text{Cl}^-$ titration (Table 16.1).

16B. INDICATION OF THE EQUIVALENCE POINT

From the titration curves of Fig. 16.2, it may be seen that $p\text{Ag}$ and $p\text{Cl}$ undergo rapid change in the region of the equivalence point. For example, in passing from 0.1% before the equivalence point to 0.1%

after (that is, from 49.95 to 50.05 ml of standard AgNO_3), $p\text{Ag}$ passes from 5.72 to 4.28, which corresponds to a change of 1.44 $p\text{Ag}$ units or a 28-fold change in $[\text{Ag}^+]$. $[\text{Cl}^-]$ changes similarly. This is a fairly large relative change; if some easily measured property or phenomenon can be found that is a function of $[\text{Ag}^+]$, this property will also change greatly in the region of the equivalence point, and will afford an indication of this point. The steeper the titration curve in the region of the equivalence point, the sharper will be the change in the indicator phenomenon, and the more precisely it may be located.

There are several indicator phenomena suitable for the NaCl-AgNO_3 titration, all depending upon the rapid change of $p\text{Ag}$ (or $p\text{Cl}$) in the region of the equivalence point. These different modes of indicating the equivalence point are outlined in the following sections, not in order of importance, but rather in order of ease in presentation. More details on some of these methods are given with the experiments and in the Supplement.

It is first necessary, however, to distinguish between the equivalence point and the end point. The *equivalence point* is the point that the observer wishes to observe and to use, for here the amount of sought-for substance may be stoichiometrically calculated from the measured amount of standard substance. However, the point that the observer actually sees is the *end point*—that point at which the indicator change occurs. The equivalence point and the end point are not necessarily identical. In a good method the end point falls so close to the equivalence point that the two are regarded as identical within experimental error, or, if there is a significant difference between the two points, this difference is reproducible and may be corrected for.

A good end point should have the following properties: (1) It should be sharp and easily perceptible. (2) It should occur at or very close to the equivalence point; otherwise there is a significant end-point error. (3) The indicator change should be reversible. Where the titrant falls into the titrated solution, a local excess of titrant may be built up, and may cause the indicator change to occur locally, even though the equivalence point has not yet been attained throughout the whole solution. When the solution is stirred, this prematurely changed indicator must quickly revert to its original state. If the indicator change is not reversible, the end point may be diffuse and premature.

16B.1. Cessation of Precipitate Formation

If, in the titration of NaCl with standard AgNO_3 , the titrated solution is allowed to settle after each addition of titrant, the clear super-

nate may be examined for evidence of precipitate formation when the next drop of standard AgNO_3 is added. So long as AgCl continues to form in the clear supernate on addition of AgNO_3 , it is evident that excess NaCl still exists in the supernate, and that the equivalence point has not yet been reached. After the equivalence point, further addition of AgNO_3 causes no further precipitation. The end point is taken as the buret reading before that drop of AgNO_3 that produces no significant turbidity in the supernate.

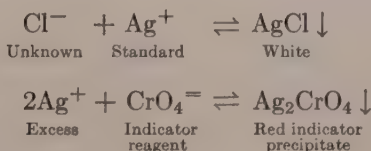
Examination of Fig. 16.2 shows that there is no sharp demarcation between two successive drops of AgNO_3 . Actually, the proportion of the added AgNO_3 precipitated in each successive drop decreases through the region of the equivalence point. In order that this decrease may be sharp, the precipitate must be very insoluble.

Because of the tediousness of performing titrations in this way, this method is of little importance today. It was used in modified form by Gay-Lussac before 1832. However, this procedure is not so troublesome as first thought might indicate. In the region of the equivalence point, the particles lose their charge, and coagulation occurs very easily. Thorough swirling of the titrated solution after each addition of standard AgNO_3 brings about coagulation of the AgCl to dense white flocs that settle rapidly, leaving a clear supernate.

A refinement of this method of titration, called the "method of equal turbidity," is extremely accurate and is used in atomic-weight work (C2, S8). Near the equivalence point, two small portions of the supernate are withdrawn. The Cl^- in one portion is precipitated by the addition of an excess of AgNO_3 , whereas the Ag^+ in the other portion is precipitated by the addition of an excess of NaCl . If the two portions are withdrawn at the end point, $[\text{Ag}^+] = [\text{Cl}^-]$, and the turbidities produced in the two portions are equal. Comparison of the turbidities is made in a nephelometer, which permits detection of rather small turbidity differences.

16B.2. Formation of a Colored Precipitate

Suppose that some K_2CrO_4 is added to a solution of NaCl that is to be titrated with standard AgNO_3 . Since Ag_2CrO_4 is more soluble than AgCl , the added Ag^+ reacts with Cl^- rather than CrO_4^{2-} up to the equivalence point. After the Cl^- is precipitated quantitatively as AgCl , the first slight excess of Ag^+ added beyond the equivalence point precipitates CrO_4^{2-} as intensely red Ag_2CrO_4 , giving the end point. This is one of the oldest titration methods in existence, described by Mohr in 1856. The method may be summarized as follows:



More precise reasoning, when Fig. 16.2 is used, shows that Ag_2CrO_4 precipitates when $[\text{Ag}^+]$ rises sufficiently high to exceed K_s for Ag_2CrO_4 . $[\text{CrO}_4^{2-}]$ may be chosen so that Ag_2CrO_4 forms when $[\text{Ag}^+]$ reaches any desired value on the titration curve (within certain practical limits), as shown in the two following examples.

Example 1. At what value must $[\text{CrO}_4^{2-}]$ be set so that Ag_2CrO_4 will just begin to precipitate at the equivalence point in the titration of 50.00 ml of 0.1000 *M* NaCl with 0.1000 *M* AgNO_3 ? (Use K_s values from Appendix V; do not use rounded values as in the titration of Fig. 16.2.)

At the equivalence point, $[\text{Ag}^+] = [\text{Cl}^-]$, and the solubility-product expression gives

$$[\text{Ag}^+]_{\text{eq pt}} = \sqrt{1.78 \times 10^{-10}} = 1.33 \times 10^{-5} \text{ } M$$

If Ag_2CrO_4 is to precipitate at the equivalence point, then

$$\begin{aligned}
 [\text{Ag}^+]^2[\text{CrO}_4^{2-}] &= 1.29 \times 10^{-12} \\
 [\text{CrO}_4^{2-}] &= \frac{1.29 \times 10^{-12}}{[\text{Ag}^+]^2_{\text{eq pt}}} = \frac{1.29 \times 10^{-12}}{(1.33 \times 10^{-5})^2} = 0.0072 \text{ } M
 \end{aligned}$$

Example 2. Actually, 0.0072 *M* K_2CrO_4 gives too yellow a color to the solution, and masks the end-point color change. For this reason, it is better to set $[\text{CrO}_4^{2-}]$ much lower—at 0.0020 *M*. Estimate the end-point error in this case.

At the end point, where Ag_2CrO_4 begins to form, and where $[\text{CrO}_4^{2-}] = 0.0020 \text{ } M$,

$$[\text{Ag}^+]^2[\text{CrO}_4^{2-}] = 1.29 \times 10^{-12}$$

$$[\text{Ag}^+]_{\text{end pt}} = \sqrt{\frac{1.29 \times 10^{-12}}{[\text{CrO}_4^{2-}]_{\text{end pt}}}} = \sqrt{\frac{1.29 \times 10^{-12}}{0.0020}} = 2.54 \times 10^{-5} \text{ } M$$

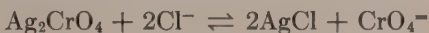
$[\text{Cl}^-]_{\text{end pt}}$ may be calculated from $[\text{Ag}^+]_{\text{end pt}}$, using the solubility product for AgCl .

$$[\text{Cl}^-]_{\text{end pt}} = \frac{1.78 \times 10^{-10}}{[\text{Ag}^+]_{\text{end pt}}} = \frac{1.78 \times 10^{-10}}{2.54 \times 10^{-5}} = 0.70 \times 10^{-5} \text{ } M$$

At the end point, the excess of Ag^+ over Cl^- is $2.54 \times 10^{-5} - 0.70 \times 10^{-5}$, or $1.8 \times 10^{-5} \text{ } M$, which represents the titration error, since there should be no excess of Ag^+ over Cl^- at the equivalence point. The titration error is the volume of 0.1000 *M* AgNO_3 required to build up this excess in 100 ml of solution, or $1.8 \times 10^{-5} \times 100/0.1000$, or 0.018 ml. Since the equivalent volume of AgNO_3 titrant is 50.00 ml, the relative end-point error is about 0.04%.

Consideration of activity effects approximately doubles this estimate.

The requirements for a satisfactory indicator precipitate should be clear from the preceding discussion and examples. (1) The indicator precipitate must be highly colored; otherwise too high an excess of AgNO_3 must be used to form a perceptible precipitate. (2) The indicator precipitate must have a suitable solubility. The Ag_2CrO_4 is of such a solubility that a convenient concentration of K_2CrO_4 causes formation of Ag_2CrO_4 close to the equivalence point. If the Ag_2CrO_4 were too insoluble (or too soluble), Ag_2CrO_4 would precipitate too far before (or after) the equivalence point, resulting in a large end-point error. The steeper the titration curve in the region of the equivalence point, the easier it is to meet this solubility requirement. As shown in the examples above, even when $[\text{CrO}_4^{2-}]$ is several times less than that required to make the end point and equivalence point coincide, the error is still less than 0.1%. The less steep the titration curve, the more critical becomes the choice of the indicator reagent concentrations, and small departures from the critical value may cause appreciable errors. (3) The indicator precipitate must be rapidly and easily formed and dissolved. As the end point is approached, Ag_2CrO_4 is formed locally and momentarily where the AgNO_3 titrant drops into the solution, but this precipitate must redissolve on stirring according to the reaction



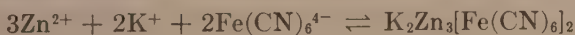
This dissolution must occur readily at concentrations of Cl^- that are very low near the equivalence point; otherwise an indistinct and premature end point will be obtained. As a matter of fact, Ag_2CrO_4 is exceptional in the rapidity with which it redissolves. Most indicator precipitates not only dissolve slowly, but also tend to become coated with the sought-for precipitate, impeding the dissolution process even more. As a consequence, there are very few precipitation indicators that may be used internally—that is, in the solution being titrated.

The Mohr titration is outlined in this section only to illustrate one type of precipitation indicator. Interferences, limitations, and conditions that must be met to obtain accurate results are discussed in Exp. 16.5 (p. 303).

16B.3. External Indicators

If a precipitation indicator cannot be used internally because it does not form and dissolve easily, it may be used externally. The external indicator technique is of only historical interest today, because it is rather tedious.

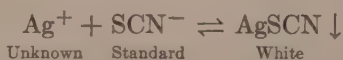
Zn^{2+} may be titrated with standard $\text{K}_4\text{Fe}(\text{CN})_6$:



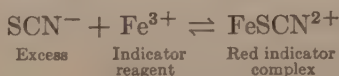
There are several cations that form insoluble colored ferrocyanides, and that meet solubility requirements for a good precipitation indicator. But if any of these—such as UO_2^{2+} , which forms $(\text{UO}_2)_2\text{Fe}(\text{CN})_6$ —is put into the titrated solution, the indicator precipitate is then formed locally long before the equivalence point is reached, and does not redissolve at an appreciable rate. Instead, the following technique is used. When it is suspected that the titration is near the equivalence point, a small drop of the titrated solution is withdrawn and mixed with a drop of dilute $\text{UO}_2(\text{NO}_3)_2$ on a white porcelain plate. If the system has not yet reached the equivalence point, Zn^{2+} is in excess, and the concentration of $\text{Fe}(\text{CN})_6^{4-}$ is so low that the solubility product of $(\text{UO}_2)_2\text{Fe}(\text{CN})_6$ is not exceeded. In this case, another small portion of standard $\text{K}_4\text{Fe}(\text{CN})_6$ is added, and the test is repeated with a fresh droplet of the titrated solution. As soon as the equivalence point is passed, an excess of $\text{Fe}(\text{CN})_6^{4-}$ exists in the titrated solution, and the red indicator precipitate of $(\text{UO}_2)_2\text{Fe}(\text{CN})_6$ is formed in the test droplet. In practice, one or two preliminary titrations are made on aliquots of the sample, with fairly large additions of standard $\text{K}_4\text{Fe}(\text{CN})_6$ between the spot tests, to bracket the end point approximately. The last titration is then carried out on another aliquot of the sample by making tests between dropwise additions of standard $\text{K}_4\text{Fe}(\text{CN})_6$ only in the region of the end point. Small portions withdrawn near the equivalence point do not contain significant amounts of the sought-for substance, and usually need not be corrected for.

16B.4. Formation of a Soluble Colored Complex

Suppose that some $\text{Fe}(\text{NO}_3)_3$ is placed in a solution of AgNO_3 that is to be titrated with standard KSCN . Up to the equivalence point, very insoluble white AgSCN is formed.



The first slight excess of KSCN added past the equivalence point reacts with the Fe^{3+} indicator ion to form the intensely red complex, FeSCN^{2+} .



This is the Volhard method for determining Ag. It is described in this section only to illustrate a soluble complex indicator. The interferences, limitations, and applications of this very important and versatile method are given in Exps. 16.3 and 16.4 (pp. 298, 301).

There are three requirements for a satisfactory indicator of this type. (1) The complex must be highly colored; otherwise, too large an excess of reagent must be used to give a perceptible color. (2) The colored FeSCN^{2+} complex must have a suitable stability, so that a convenient concentration of Fe^{3+} indicator ion causes color formation close to the equivalence point. If the FeSCN^{2+} were too stable (or too unstable), color formation would occur too far before (or after) the equivalence point, resulting in a large end-point error. The steeper the titration curve in the region of the equivalence point, the easier it is to satisfy this requirement, as shown in the illustrative examples below. (3) Easy reversibility of formation and dissociation of the complex is necessary. This requirement is easier to meet for complexation indicators than for precipitation indicators, since the rates of dissociation and formation of most soluble inorganic complexes are much higher than the rates of formation and dissolution of precipitates.

Example 1. Suppose that $[\text{Fe}^{3+}]$ is set to be 1.0 *M* in performing a Volhard titration of 50.00 ml of 0.1000 *M* AgNO_3 with 0.1000 *M* KSCN . What is the end-point error? Assume that K_s for AgSCN is 1.07×10^{-12} , and that the FeSCN^{2+} formation constant is 1070. The minimum concentration of FeSCN^{2+} required for a visible coloration is 6.4×10^{-6} *M*.

At the end point, $[\text{SCN}^-]$ may be calculated from the FeSCN^{2+} formation constant.

$$\frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} = 1070$$

$$[\text{SCN}^-]_{\text{end pt}} = \frac{[\text{FeSCN}^{2+}]_{\text{end pt}}}{1070 \times [\text{Fe}^{3+}]_{\text{end pt}}} = \frac{6.4 \times 10^{-6}}{1070 \times 1.0} = 5.97 \times 10^{-9} \text{ M}$$

From $[\text{SCN}^-]_{\text{end pt}}$ and the solubility-product expression, $[\text{Ag}^+]_{\text{end pt}}$ may be calculated.

$$[\text{Ag}^+][\text{SCN}^-] = 1.07 \times 10^{-12}$$

$$[\text{Ag}^+]_{\text{end pt}} = \frac{1.07 \times 10^{-12}}{[\text{SCN}^-]_{\text{end pt}}} = \frac{1.07 \times 10^{-12}}{5.97 \times 10^{-9}} = 1.79 \times 10^{-4} \text{ M}$$

Now the end-point error may be calculated. For no error, the total millimoles of silver in the system should be identical to the total millimoles of thiocyanate added. The end-point error may be calculated as the discrepancy between the total silver and the total thiocyanate in the system at the end point.

$$\left(\begin{array}{c} \text{End-pt. error, or} \\ \text{mmoles of Ag}^+ \text{ in} \\ \text{excess over mmoles SCN}^- \end{array} \right) = \left(\begin{array}{c} \text{total mmoles} \\ \text{of Ag}^+ \text{ present} \end{array} \right) - \left(\begin{array}{c} \text{total mmoles} \\ \text{of SCN}^- \text{ present} \end{array} \right)$$

$$= (\text{mmoles Ag}^+ \text{ in ppt}^* + \text{mmoles Ag in soln.})$$

$$- (\text{mmoles SCN}^- \text{ in ppt}^* + \text{mmoles SCN}^- \text{ and FeSCN}^{2+} \text{ in soln.})$$

*The mmoles of Ag^+ in the precipitate of AgSCN are of course identical to the mmoles of SCN^- in the precipitate.

$$\begin{aligned}
 &= \text{mmoles Ag}^+ \text{ in soln.} - \text{mmoles SCN}^- - \text{mmoles FeSCN}^{2+} \\
 &= 1.79 \times 10^{-4} \times 100 - 5.97 \times 10^{-9} \times 100 \\
 &\quad - 6.4 \times 10^{-6} \times 100 \\
 &= 0.018 \text{ mmoles}
 \end{aligned}$$

Since Ag^+ is in excess, the end point comes before the equivalence point. The difference between the two points, in terms of 0.1000 M KSCN standard solution, is 0.018/0.1000, or 0.18 ml. Compared to the equivalence-point volume of 50.00 ml of 0.1000 M KSCN, the relative error is -0.4% .

Example 2. What must $[\text{Fe}^{3+}]$ be, in order that the FeSCN^{2+} color will appear just at the equivalence point in the titration of Ex. 1?

At the equivalence point,

$$\begin{aligned}
 \left(\begin{array}{c} \text{Total mmoles silver} \\ \text{in the system} \end{array} \right) &= \left(\begin{array}{c} \text{total mmoles SCN}^- \\ \text{in the system} \end{array} \right) \\
 \left(\begin{array}{c} \text{mmoles Ag}^+ \text{ in ppt}^* \\ + \text{mmoles Ag}^+ \text{ in soln.} \end{array} \right) &= \left(\begin{array}{c} \text{mmoles SCN}^- \text{ in ppt}^* + \text{mmoles} \\ \text{SCN}^- \text{ and FeSCN}^{2+} \text{ in soln.} \end{array} \right)
 \end{aligned}$$

At the equivalence point, since concentrations are proportional to amounts,

$$\begin{aligned}
 [\text{Ag}^+] &= [\text{SCN}^-] + [\text{FeSCN}^{2+}] \\
 \frac{1.07 \times 10^{-12}}{[\text{SCN}^-]} &= [\text{SCN}^-] + 6.4 \times 10^{-6}
 \end{aligned}$$

This equation may be solved for $[\text{SCN}^-]$ with the quadratic formula or by approximations,

$$[\text{SCN}^-]_{\text{eq pt}} = 0.163 \times 10^{-6} M$$

Now the $[\text{Fe}^{3+}]$ required to give the perceptible concentration of FeSCN^{2+} just at the equivalence point may be found from the stability constant of FeSCN^{2+} :

$$\begin{aligned}
 \frac{[\text{FeSCN}^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} &= 1070 \\
 [\text{Fe}^{3+}] &= \frac{[\text{FeSCN}^{2+}]}{1070[\text{SCN}^-]} = \frac{6.4 \times 10^{-6}}{1070(0.163 \times 10^{-6})} = 0.037 M
 \end{aligned}$$

Comparison of this ferric-ion concentration with that used in Ex. 1 indicates that the choice of indicator concentration in the Volhard method is not at all critical. In fact, the indicator concentration in Exp. 16.3 (p. 298) is only about 0.02 M , and the end-point error is very small.

16B.5. Adsorption Indicators

Dichlorofluorescein ($\text{C}_{19}\text{H}_9\text{O}_3\text{Cl}_2 \cdot \text{COOH}$, or Hdf) is a weak organic acid.



*The mmoles of Ag^- in the precipitate of AgSCN are of course identical to the mmoles of SCN^- in the precipitate.

The dichlorofluoresceinate ion (Df^-) forms AgDf , which is deep red and moderately insoluble. For this reason Df^- tends to be adsorbed on the surface of AgCl , and, in so doing, Ag^+ and Df^- come into close enough proximity to form the colored AgDf bonds on the surface of the precipitate even though the solubility product of AgDf is not exceeded in the solution.

Suppose that the titration of NaCl with standard AgNO_3 is carried out in the presence of a low concentration of Df^- as an indicator. As long as the system has not reached the equivalence point, the AgCl exists in a solution containing excess NaCl , and is therefore negatively charged due to preferential adsorption of Cl^- . Df^- has little tendency to be adsorbed on this negatively charged precipitate, which therefore remains white. After the equivalence point is passed, the AgCl exists in excess AgNO_3 , and is positively charged, owing to preferential adsorption of Ag^+ . Here Df^- has a good tendency to be adsorbed on

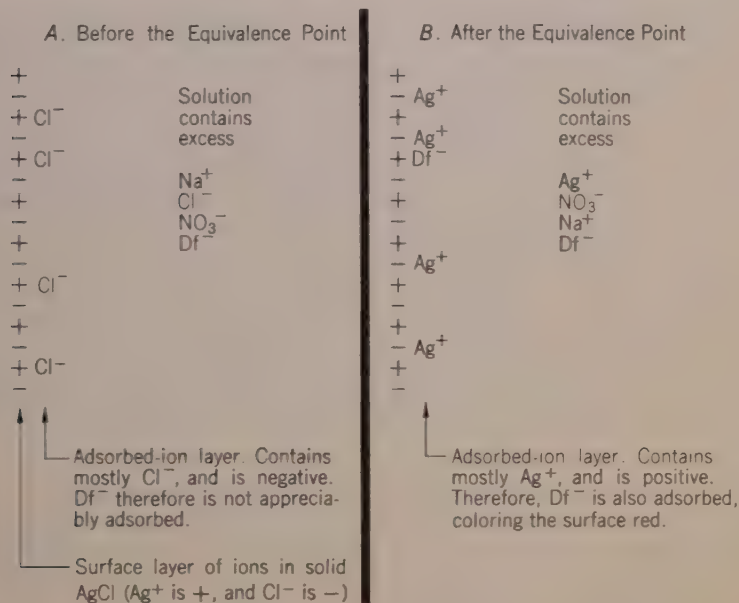


FIG. 16.5. Behavior of Dichlorofluorescein in the Titration of NaCl with AgNO_3

this positively charged precipitate, coloring it. It is in the region of the equivalence point, where $[\text{Ag}^+]$ increases and $[\text{Cl}^-]$ decreases rapidly, that the charge on the AgCl changes from negative to positive, and the color from white to red. The process is summarized in Fig. 16.5.

For proper indicator action, the precipitate must be an insoluble one, like AgCl , so that its ions are strongly adsorbed. Then, the transition from a negatively charged precipitate (in excess Cl^-) to a positively charged one (in excess Ag^+) is very sharp through the region of the equivalence point, and so is the transition from no adsorption of Df^- (white) to high adsorption of Df^- (red). The sharpness of the process is depicted in Fig. 16.6.

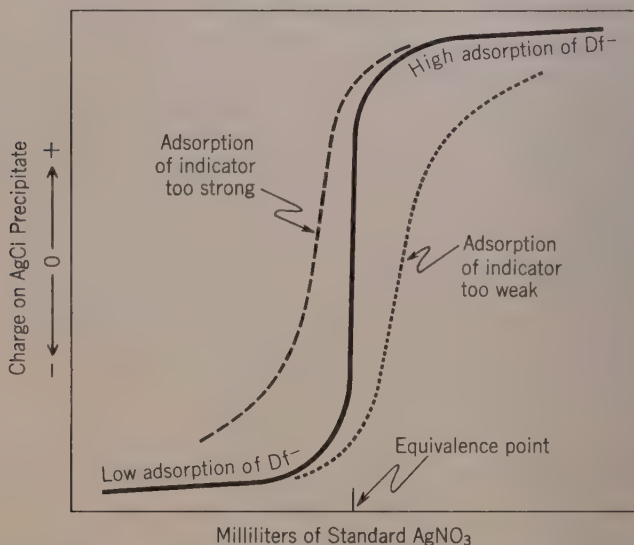


FIG. 16.6. Behavior of Dichlorofluorescein in the Titration of NaCl with AgNO_3

Also for proper indicator action, there must be a certain adsorption affinity between the indicator and precipitate.



If the indicator is adsorbed too weakly, then the end-point color change is spread out and comes late (Fig. 16.6, dotted curve). On the other hand, if the indicator is adsorbed too strongly, so that it begins to compete with Cl^- , then the indicator goes onto the precipitate too early and the end-point color change comes too soon (Fig. 16.6, dashed curve). Some control over the adsorption equilibrium is obtainable by pH control, since adsorption indicators are weak acids or bases. Thus, dichlorofluoresceinate is adsorbed a little too strongly to be usable in the fully ionized form in the $\text{Ag}^+\text{-Cl}^-$ titration. However, HDf is a weak acid ($\text{p}K_a = 4$), and by using it at $\text{pH } 4$, the Df^- activity is diminished sufficiently to make it suitable for the $\text{Ag}^+\text{-Cl}^-$ titration.

The extent to which pH may be altered to make a particular indicator suitable for a particular titration is of course limited. However, a wide selection of indicators of different acidities and adsorbabilities is available (see Supplement, p. 656).

The unique advantage of adsorption indicators is that the color changes are not only very sharp, but also very close to the equivalence point. An additional advantage is that control of pH usually permits the end point to be made coincident with the equivalence point. There are defects, however, the principal one being that high electrolyte concentrations cause displacement of the indicator and spoil the sharpness of the end point.

The use of dichlorofluorescein was first described by Fajans. The Fajans titration is discussed in this section only to illustrate an adsorption indicator. Interferences, limitations, and conditions that must be met to obtain accurate results are given in Exp. 16.2 (p. 295).

16B.6. Instrumental Methods

In the titration of $NaCl$ with $AgNO_3$ the conductance of the titrated solution may be determined at various points in the titration by measuring the current produced by a small voltage across two electrodes immersed in the solution. A plot of conductance against volume of standard $AgNO_3$ gives a *V-shaped curve* similar in form to Fig. 16.1. The sharp break is taken as the end point. Similarly, the potential of an electrode immersed in the titrated solution may be measured at various points in the titration. A plot of these potentials against volume of standard $AgNO_3$ gives an *S-shaped curve* similar in form to Fig. 16.2. The end point is taken as the midpoint of the region of steepest slope. A few other instrumental methods are mentioned in Chapter 22.

16C. OTHER PRECIPITATION TITRATIONS

Not all reactions forming insoluble precipitates may be used in titrations, for most of them do not meet the requirements of a satisfactory reaction. In particular, there are two disadvantages to volumetric precipitation reactions as compared to reactions in which no precipitates are formed. (1) Coprecipitation causes error if either the sought-for or standard substance is coprecipitated as a compound other than the sought-for precipitate. Since there is always a tendency for coprecipitation of the reagent or sought-for substance, this error is always at least potentially present in precipitation processes. (2) The rate of formation of the precipitate is often a severe limitation in titrations. Under the

conditions of a titration, where the precipitant is added slowly, a high degree of supersaturation does not exist. This is particularly true as the equivalence point is approached, and for some reactions too long a wait is required for each drop of titrant to react completely.

Primarily because of these limitations, very few accurate direct titrations are based upon precipitation reactions. In fact, the argentimetric determinations of this chapter are the only ones frequently used. Extensions of the argentimetric titrations are described in the Supplement (pp. 759, 760).

There are a few direct precipitation titrations that operate around the one per cent error level; some of these are outlined in Table 16.2 (K19, Vol. II). Most precipitation titrations are indirect: a measured excess of standard precipitant is added, and after precipitation, the excess is back-titrated with a second standard solution. The indirect procedure avoids difficulties of low rates of precipitation; also, if desirable, the precipitate may be removed before the back titration.

TABLE 16.2
SOME PRECIPITATION TITRATIONS

Sought-for Substance	Titrant	Titration Medium	Indicator	Titration Product	Notes
Zn ²⁺1 M K ⁴ Fe(CN) ₆	0.5 M HCl, 0.5 M NH ₄ Cl, 80°C	UO ₂ (NO ₃) ₂ (external)	K ₂ Zn ₃ Fe(CN) ₆	1
Th ⁴⁺002 M (NH ₄) ₂ MoO ₄	pH 1.8	Amperometric	Th(MoO ₄) ₂	
Th ⁴⁺02 M H ₂ C ₂ O ₄	pH 3.5, 60°C	Dinitroso- chromotropic acid	Th(C ₂ O ₄) ₂	2
Pb ²⁺01 M (NH ₄) ₂ MoO ₄	pH 4	Eosin, etc. (adsorption)	PbMoO ₄	
SO ₄ ⁻01 M Ba(ClO ₄) ₂	80% alcohol, pH 2.5-4	Thorin	BaSO ₄	2, 3, 4
SO ₄ ⁻01 M Pb(NO ₃) ₂	80% acetone, pH 4	Dithizone	PbSO ₄	2, 3, 5
F ⁻01 M Th(NO ₃) ₄	pH 3	Alizarin red S	ThF ₄	6
PO ₄ ⁼01 M UO ₂ (NO ₃) ₂	20% alcohol, pH 3.5	Amperometric	KUO ₂ PO ₄	7

(1) About 1% less than the stoichiometrical amount of K₄Fe(CN)₆ is required, but the error is highly reproducible and may be compensated for in standardization. Elevated temperature hastens equilibration of the precipitate with the solution. Indicator action is described on page 283. The end point may also be established potentiometrically. Cd²⁺ may be titrated similarly.

(2) These indicators are metallochromic ones, and form complexes with the metal ions that differ in color from the uncomplexed indicators. The color changes in passing through the end points are: dinitrosochromotropic acid, violet to red; thorin, yellow-orange to pink; dithizone, green to red.

(3) Most cations interfere, but may be removed by ion exchange before titration.

(4) The alcoholic medium yields a gelatinous precipitate that equilibrates very rapidly, unlike the crystalline precipitate that forms in aqueous medium.

(5) The acetone medium reduces the solubility of PbSO₄ to give a sharper end point, and also holds dithizone and its lead complex in solution.

(6) The indicator is yellow, and changes to a red thorium alizarin lake at the end point.

(7) Alcohol reduces the solubility of the KUO₂PO₄ to give a sharper end point.

16D. EXPERIMENTS

The following five experiments are all argentimetric titrations. In Exp. 16.1, primary standard AgNO_3 and KSCN solutions are prepared and checked by titration against each other. Experiment 16.1 should not be omitted. These standard solutions are then used to determine chloride by the Fajans method (Exp. 16.2), silver by the Volhard method (Exp. 16.3), and chloride by the Volhard method (Exp. 16.4). In Exp. 16.5 chloride is determined by the Mohr method, but the AgNO_3 titrant is empirically standardized with primary standard NaCl . Preparation of unknown samples is described in the Supplement (p. 763).

Volumetric techniques are described in Chapter 15, which should be studied critically before any of the following titrations are undertaken.

EXPERIMENT 16.1. PREPARATION OF STANDARD AgNO_3 AND KSCN SOLUTIONS

Standard 0.1 M AgNO_3 and KSCN solutions are prepared from the reagent-grade substances as primary standards. These two solutions are then checked by titration against each other, both the Fajans and the Volhard methods being used. The purpose of this check is to verify the correctness of the standard solutions and of the student's technique before proceeding to the analysis of unknown samples. There is no unknown sample in this experiment.

PROCEDURE

1. Prepare 500 ml each of 0.1 M AgNO_3 and 0.1 M KSCN from the primary standard substances. (a) With the platform balance, weigh 10% more of the analyzed-grade reagent than is required into a small, clean, dry weighing bottle. (Notes 1, 2.) (b) Dry in the electric oven at 105–110°C for 2 hours. Cool for one hour before weighing. (Notes 3, 4, 5.) (c) To the nearest milligram, weigh into a clean, dry, 150-ml beaker enough substance to prepare 500 ml of 0.095–0.105 M solution. (Note 6.) (d) Flush all substance quantitatively into the volumetric flask, using a funnel and wash bottle to effect the transfer. After all substance is dissolved, dilute to the mark and mix well. Store the solution in a narrow-mouthed glass-stoppered bottle, and label properly. (Notes 7, 8.) (e) Compute the molarity. (Notes 9, 10, 11.)

2. By the Fajans method, titrate duplicate 35-ml portions of the standard KSCN with the standard AgNO_3 . (Run a 35-ml portion of the KSCN into a 250-ml Erlenmeyer flask, add 15 ml of water, and titrate as in Exp. 16.2, step 3. Do not add HAc-NaAc buffer.) Calculate the average volume of AgNO_3 required per milliliter of KSCN .

3. By the Volhard method, titrate duplicate 35-ml portions of the standard AgNO_3 with the standard KSCN . (Run a 35-ml portion of the AgNO_3 into a 250-ml Erlenmeyer flask, and add 25 ml of water and 5 ml of a 1:1 HNO_3 solution that has been boiled for a few minutes to remove nitrogen oxides. Titrate as in Exp. 16.3, steps 2, 3.) Calculate the average volume of AgNO_3 required per milliliter of KSCN .

4. Computations. (a) Calculate the average of the two volumes of AgNO_3 required per milliliter of KSCN , calling the over-all average V . (Notes 12, 13.) (b) From V and M_{KSCN} there may be calculated a second estimate of the AgNO_3 molarity, which is equal to M_{KSCN}/V , and which should agree with M_{AgNO_3} within 0.1% for excellent work. (Note 14.) The best estimate of the standard AgNO_3 molarity is the average of M_{AgNO_3} and M_{KSCN}/V . (c) The best estimate of the standard KSCN molarity is the average of M_{KSCN} and VM_{AgNO_3} , which should agree within 0.1% for excellent work. (Notes 14, 15.)

NOTES

(1) For this experiment and any one of the following, 500 ml of each solution should suffice. If more than one of the following experiments are to be done, prepare 1 l of the AgNO_3 .

(2) The rough weight of AgNO_3 that should be taken to prepare 500 ml of 0.100 M solution is

$$0.100 \times 500 \left| \times 1.10 \right| \times \frac{170}{1000} = 9.3 \text{ g}$$

10% excess

mmoles AgNO_3 for 500 ml

The rough weight of KSCN should be calculated similarly.

(3) Normally, samples to be dried are ground to a fineness comparable to that of granulated sugar, to hasten removal of occluded water. This practice is not followed here because of the danger of contamination in grinding. Large lumps may be fractured in the weighing bottle by applying slight pressure with the end of a fire-polished glass rod. The preparation and testing of primary standard-grade NaCl , KCl , KBr , KSCN , and AgNO_3 are described in detail by Kolthoff and Stenger (K19). To prepare these substances for reliable use much below the 0.1% error level requires considerable effort in purification. Also, the last few hundredths of a per cent of water can only be removed at rather high temperatures. At the 0.1% error level, however, analyzed reagent-grade chemicals are adequate after drying at 105–110°C for 2 hours. The solutions are all stable.

(4) Slight discoloration of the AgNO_3 upon heating is caused by organic matter, but is of no consequence. Paper-labeled containers or other organic matter should not be put in the oven, for they might cause appreciable reduction of AgNO_3 . Reagent KSCN is hygroscopic. If a damp preparation is dried at elevated temperature, it fuses to a solid mass that is troublesome to remove from the weighing bottle. It is recommended that the instructor remove excess moisture by heating the KSCN in the reagent bottle at 60–80°C overnight. If the amount of moisture is not excessive, the contents may be chopped up without removal from the bottle, to give a granulated preparation. The bottle should be labeled for special use, and should be

kept securely capped at all times, except when removing reagent. Such a preparation may be dried at 100–110°C by students with no danger of fusion.

(5) If the substance is to be weighed out within a few hours after drying, it is desirable to cool the stoppered bottle in air. For long storage times, the desiccator should be used.

(6) The range of weights of AgNO_3 that may be used is from $0.095 \times 170 \times 500/1000 = 8.1$ g to $0.105 \times 170 \times 500/1000 = 8.9$ g. The range of weights of KSCN should be calculated similarly. With more trouble, the amounts required to prepare precisely 0.1000 *M* solutions may be weighed into tared 150-ml beakers. This saves time in computations, but is not recommended unless the student has good weighing technique. KSCN is hygroscopic at humidities over 50%.

(7) Test a 10-ml portion of the distilled water for chloride after acidification with 1 drop of conc. HNO_3 by adding a drop of 0.5 *M* AgNO_3 . If more than the faintest turbidity develops, do not use the water. Reject the test portion.

(8) The identifying label should contain the name and concentration of the reagent, the temperature and date of standardization, and the initials of the worker. If the interior of the bottle is not dry, it must be rinsed with several small portions of the solution to be placed therein. The rinsings must be rejected.

(9) The molarity is

$$\frac{\text{mg of substance}}{\text{MW of substance}} \times \frac{1}{\text{vol. of flask, ml}} = \frac{\text{mmoles}}{\text{mmoles per ml}}$$

(10) If the laboratory temperature varies less than 5°C from day to day, no temperature corrections need be applied. If the variation is greater than 5°C, all concentrations and volumes should be corrected to a mean temperature.

(11) To prevent confusion in reporting and discussing results, it is suggested that the same symbols be used by all members of the class. Let the molarities of the two solutions, as calculated from the weight of primary standard substances used, be symbolized by M_{AgNO_3} and M_{KSCN} .

(12) The ratio of the volumes required in titration should be inverse to the ratio of the concentrations. Thus V , which is the milliliters of AgNO_3 per milliliter of KSCN , should be the same as $M_{\text{KSCN}}/M_{\text{AgNO}_3}$.

(13) Up to this point three measurements have been made: M_{AgNO_3} , M_{KSCN} , and V , which is $M_{\text{KSCN}}/M_{\text{AgNO}_3}$. There are several ways of calculating the two standard solution concentrations from these three data. To prevent confusion, it is suggested that the symbols and method of step 4 be used by all members of the class. This method weights each of the three data equally.

(14) Often the discrepancy is greater than 0.1%, and the question then arises as to what should be done. Ideally, if it is the objective of the student to do excellent work, the only proper course is to resolve the discrepancy and to work until the required precision is obtained. (In favor of this course, it should be stated that errors are often found and resolved quickly by observant searching.) This course cannot always be followed, because time is limited. Two alternatives are possible. (a) A discrepancy of 0.2–0.4% may be accepted as passable, with the expectation that this will probably also be the error made in analysis of unknown samples. (b) One of the three data (M_{AgNO_3} , M_{KSCN} , or V) may be rejected, and the “best” standard solution concentrations calculated from the remaining two. If the reason for rejection is valid, this is a proper course of action, but it is insufficient, for there is no assurance that the remaining data are accurate.

(15) An example of a summary data page will be found on page 294.

SUMMARY DATA PAGE

EXP. 16.1. PREPARATION OF STANDARD AgNO_3 AND KSCN

Date begun.....

John Brown

Date completed.....

Locker No.....

Prepn. of Solutions (Data, p.)	AgNO_3	KSCN
Grams pri. std. substance		
Vol. of flask, ml		
Molarity (M_{AgNO_3} and M_{KSCN})		

Titration of solutions	Detn.	ml AgNO_3	ml KSCN	$\frac{\text{ml } \text{AgNO}_3}{\text{ml } \text{KSCN}}$
Fajans (Data, p.)	1			
	2			
	3			
	Av. ml AgNO_3 per ml KSCN			
Volhard (Data, p.)	1			
	2			
	3			
	Av. ml AgNO_3 per ml KSCN			

Calculations

Over-all average ml AgNO_3 per ml KSCN , or V
 M_{KSCN}/V M
 VM_{AgNO_3} M
 Best AgNO_3 conc. $(M_{\text{AgNO}_3} + M_{\text{KSCN}}/V)/2$ M
 Best KSCN conc. $(M_{\text{KSCN}} + VM_{\text{AgNO}_3})/2$ M
 Rel. diff. $\frac{(M_{\text{AgNO}_3} - M_{\text{KSCN}}/V)}{M_{\text{AgNO}_3}} \times 1000$ p.p.t.

EXPERIMENT 16.2. THE FAJANS TITRATION OF CHLORIDE

The chloride content of a sample containing only NaCl and KCl is determined by direct titration with standard AgNO_3 , using dichlorofluorescein as an adsorption indicator. The reaction is stoichiometric, and the end-point error is negligible. Other adsorption indicators and their uses are given in the Supplement (p. 756).

THEORY

The mechanism for the color change of an adsorption indicator was given on page 287. The following facts are also pertinent to an understanding of the Fajans method.

Indicator concentration. Only a trace of indicator is needed; often 10^{-3} – 10^{-4} mole of indicator per mole of precipitate is sufficient. At the end point an appreciable fraction of the indicator will be adsorbed to give the color change.

Acidity. With dichlorofluorescein, the titration must be carried out at pH 4–10. Above this range, precipitation of AgOH may occur. Below this range, ionization of the dichlorofluorescein is repressed by the high acid concentration, and adsorption of the indicator is decreased.

Stirring. Chloride is probably adsorbed upon the first portions of AgCl formed, and thorough agitation is necessary to aid desorption and to prevent occlusion. With occlusion of chloride the end point will be premature, the reproducibility poor, and the Cl content low. With good stirring, the end point may be reproduced within a few hundredths of a milliliter of 0.1 M AgNO_3 .

Ionic strength and temperature. For the end point to be perceptible, it is necessary that the AgCl have a high specific surface (i.e., be colloidal). There is a tendency, however, for the AgCl to coagulate near the end point, reducing the intensity of the color change. This difficulty is not so great with fluorescein or dichlorofluorescein, but is marked with eosin. In order to stabilize the colloidal state, dextrin or polyethylene glycol is sometimes added as a protective colloid.

At high concentrations of foreign electrolyte not only is the tendency toward coagulation increased, but there may also be displacement of the adsorbed indicator ions by those of the foreign electrolyte. The end points for dichlorofluorescein and many other adsorption indicators become progressively less distinct as the ionic strength increases above 0.1 M.

At higher temperatures not only is the tendency toward coagulation increased, but the adsorption of the indicator ion is reduced also, both effects reducing the sharpness of the end point.

Chloride concentration. At chloride concentrations above 0.1 *M*, the dichlorofluorescein end point is not only indistinct, but it also appears to come about 1% before the equivalence point. At chloride concentrations below 0.005 *M*, the end point also becomes less distinct because there is not enough precipitate (and hence not enough surface for adsorption of the indicator) to give a sharp end point. At 0.0005 *M* chloride, the standard deviation is 1–2%. For chloride concentrations outside the range of 0.1–0.005 *M*, the Volhard and Mohr methods are superior to the Fajans.

Light. Adsorption of fluorescein or its derivatives makes AgCl more sensitive toward photodecomposition, which blackens the precipitate and interferes with perception of the color change. Titrations cannot be carried out in sunlight. Diffuse daylight or artificial light must be used.

Chemical interferences. The Fajans method is subject to many interferences. Most cations except the alkalis and alkaline earths interfere in several ways. (1) Some, such as Fe^{3+} , form insoluble colored hydroxides in neutral or slightly acid solution. (2) Some, such as Al^{3+} and Fe^{3+} , hydrolyze to insoluble basic salts in neutral or slightly acid solution, showing a tendency to coprecipitate chloride. (3) NH_4^+ interferes if the *pH* is above 7. Here the NH_3 formed increases the solubility of AgCl, making the end point indistinct.

TABLE 16.3
SOLUBILITIES OF VARIOUS SILVER SALTS*

INSOLUBLE IN NEUTRAL SOLUTION		SOLUBLE IN NEUTRAL OR ACID SOLUTION
Insoluble in Acid†	Soluble in Acid	
AgBr	Ag_3AsO_4	$\text{AgC}_2\text{H}_3\text{O}_2^\ddagger$
AgCN	$\text{Ag}_2\text{B}_4\text{O}_7$	AgClO_3
$\text{Ag}_3\text{Fe}(\text{CN})_6$	Ag_2CO_3	AgF
$\text{Ag}_4\text{Fe}(\text{CN})_6$	Ag_2CrO_4	AgNO_2^\ddagger
AgIO_3	$\text{Ag}_2\text{C}_2\text{O}_4$	AgNO_3
AgI	Ag_3PO_4	AgClO_4
Ag_2S	Ag_2SO_3	AgMnO_4^\ddagger
AgSCN		$\text{Ag}_2\text{SO}_4^\ddagger$
		AgBrO_3^\ddagger

*Data taken from E. H. Swift, *Introductory Quantitative Analysis* (Englewood Cliffs, N. J.: Prentice-Hall, Inc., 1950), Table 7, with permission of the publisher.

†All except AgIO_3 are less soluble than AgCl.

‡Only moderately soluble.

Table 16.3 classifies anions according to the solubilities of their Ag salts. All anions forming Ag salts insoluble in neutral solution cause error, for they react with standard AgNO_3 in the same way as chloride.

Theoretically, conditions could be selected to tolerate moderate concentrations of some anions whose Ag salts are soluble in neutral or acid solution. However, there is still a tendency for these anions to coprecipitate, even when the solubility products of the Ag salts are not exceeded. This tendency exists even for anions forming moderately soluble Ag salts, such as sulfate and nitrite. If any such anions are present in a chloride sample, a study should be made of the concentration levels at which each may be tolerated. It should not be assumed that there is no interference simply because the Ag salts are soluble.

Colored compounds of any sort obscure the end point, which is taken as the faintest tinge of pink detectable on the white AgCl precipitate. Some organic substances, such as formaldehyde, interfere by reducing Ag^+ , but these are easily removed by previous oxidation.

PROCEDURE

1. Dry sample 2 hours at 105–110°C.
2. To the nearest 0.1 mg, weigh out 1.1–1.3 g of sample and dilute to volume in the 250-ml volumetric flask. (Notes 1, 2.) Titrate 50-ml aliquots of this solution.
3. To the 50-ml sample aliquot in a 250-ml Erlenmeyer flask, add 1 ml of 0.5 *M* HAc–0.5 *M* NaAc buffer, 10 ml of 1% dextrin solution, and 5 drops of dichlorofluorescein indicator solution. Titrate with standard 0.1 *M* AgNO_3 , swirling constantly during addition of the AgNO_3 . (Notes 3–5.)
4. Perform the titration in triplicate. (Notes 6, 7.)
5. Calculate the average volume of AgNO_3 used per 50-ml aliquot of sample solution. Report the average % Cl in the sample. (Note 8.)

NOTES

(1) The sample size should be chosen so that 30–45 ml of 0.1 *M* AgNO_3 are required for titration. The composition must be approximately known for this choice. For NaCl–KCl mixtures the sample size is reckoned as follows:

For 45 ml of 0.100 *M* AgNO_3 , the weight of pure NaCl required is $0.100 \times 58.45 \times 45/1000 = 0.263$ g NaCl in a 50-ml aliquot, or $0.263 \times 250/50 = 1.31$ g/250 ml of solution. This represents an upper limit to sample size, for if 1.31 g of a KCl sample is taken, less than 45 ml AgNO_3 will be required.

For 30 ml of 0.100 *M* AgNO_3 , the weight of pure KCl required is $0.100 \times 74.56 \times 30/1000 = 0.224$ g KCl in a 50-ml aliquot, or $0.224 \times 250/50 = 1.12$ g/250 ml of solution. This represents a lower limit to the sample size, for if 1.12 g of an NaCl sample is chosen, more than 30 ml AgNO_3 will be required.

If samples of different composition are used, the instructor will announce the proper sample size.

(2) The NaCl–KCl unknowns of the elementary course are neutral, and the acidity need not be adjusted at this point. If a sample solution is acid, it should be neutral-

ized with NaHCO_3 to pH 4–6. If a sample solution is basic, it should first be made slightly acid with HNO_3 , and then neutralized with NaHCO_3 . If much NaHCO_3 is used, a control titration should be run with the same amount of NaHCO_3 , since this reagent may contain appreciable amounts of chloride.

(3) The end point is the first sharply perceptible appearance of pink that persists while the solution is swirled. A large sheet of white paper as a background aids in detecting the color.

(4) If several minutes are required to reach the end point, photoreduction may cause the AgCl to turn gray, obscuring the end point. To avoid this difficulty, a trial titration of a 25-ml aliquot of the sample solution may be made to locate the end point approximately. On subsequent titration of each 50-ml aliquot of the sample solution, the dichlorofluorescein (but not the dextrin or HAc) is withheld until a few tenths of a milliliter before the end point. Then the indicator may be added and the titration quickly completed. When withheld in this way, the dichlorofluorescein has little opportunity to induce the photodecomposition of AgCl . (Photoreduction is not so severe a problem in titrating thiocyanate as in titrating chloride.)

(5) The dichlorofluorescein has a high tendency to be adsorbed onto the AgCl , and the end point is premature by several tenths of a per cent in neutral solution. To prevent this error, the acidity is adjusted to about pH 4 with the HAc-NaAc buffer. The increased acidity complexes the indicator, decreasing its tendency to be adsorbed on the AgCl , and causing the end point to fall very close to the equivalence point.

In the titration of thiocyanate with AgNO_3 , the acidity need not be so adjusted. Since AgSCN is more insoluble than AgCl , SCN^- is adsorbed strongly enough before the equivalence point to prevent premature adsorption of the negative dichlorofluoresceinate ion. The end-point error is negligible at pH 5–7 in the titration of thiocyanate.

(6) The relative range of triplicate titrations should be less than 0.2% for excellent work.

(7) Pour all solutions and precipitates containing Ag into the jars marked "Silver Residues."

(8) The % Cl is

$$\frac{\text{AgNO}_3 \text{ molarity} \times \text{ml AgNO}_3}{\text{mmoles AgNO}_3, \text{ or mmoles Cl}} \times 35.453 \times \frac{100}{\left(\frac{\text{mg sample}}{\text{in aliquot}} \right)} = \text{mg Cl}$$

EXPERIMENT 16.3. THE VOLHARD DETERMINATION OF SILVER IN AN ALLOY

The Ag content of an Ag-Cu alloy is determined by direct titration with standard KSCN , Fe^{3+} being used as an indicator. The reaction is stoichiometric, and the end-point error is negligible.

THEORY

The mode of indicator action was described on page 284. The following facts are also pertinent to an understanding of the Volhard method.

Indicator concentration and end-point error. Because of the low solubility of AgSCN , the titration curve is quite steep and the end-point error is small. The Fe^{3+} indicator concentration is not critical; $0.01\text{ }M$ is sufficient to give a perceptible color with a negligible excess of thiocyanate. Only about 0.01 ml of $0.1\text{ }M$ KSCN is required past the equivalence point to give the end point. The end-point error may be determined as a blank, and is independent of sample size.

Acidity. The acidity must be fairly high (about $0.3\text{ }M$); otherwise Fe^{3+} hydrolyzes (p. 769), imparting an interfering yellow color to the solution.

Stirring. The first portions of AgSCN , which are formed in excess AgNO_3 , have a great tendency to adsorb Ag^+ . Vigorous stirring is needed throughout the whole titration to prevent occlusion of soluble Ag salts. Also, near the end point, the adsorbed Ag^+ desorbs rather slowly, and with poor stirring a pseudo end point may be obtained $0.5\text{--}1\%$ before the equivalence point (K19). The true end point is very close to the equivalence point, and is attained only when the red color persists for at least a half-minute on vigorous swirling. Even with good stirring it has been shown that the desorption of Ag^+ is not complete, and that the end point still comes about 0.1% before the equivalence point. There is, however, a compensating error of about 0.08% , due to the oxidation of KSCN , so that the over-all error is still well below 0.1% (K15).

Interferences. Since the Volhard method is performed in acid solution, interferences are fewer than in the Fajans or Mohr methods. In theory, at least, moderate amounts of the anions in columns 2 and 3 of Table 16.3 may be tolerated. Metal ions do not hydrolyze in the acid solution. However, there may be other interferences. (1) Oxides of nitrogen react with thiocyanate, giving reddish products. The coloration not only obscures the end point, but also may be mistaken for it. NO_2 may be present in conc. HNO_3 , which must therefore be diluted and boiled to remove NO_2 before being used. HNO_3 itself oxidizes thiocyanate, giving NO_2 and a number of intermediate and final products, such as H_2S , S , HOCN , and HCN , some of which may interfere. These reactions do not proceed rapidly before the equivalence point, because the thiocyanate concentration is low. However, they may be speeded by elevated temperature, or near the equivalence point, where the thiocyanate concentration becomes significant. (2) Strong oxidizing agents oxidize thiocyanate. These may be reduced with Fe^{2+} , excess of which may be oxidized to Fe^{3+} by heating the HNO_3 solution. (3) Substances that precipitate thiocyanate (e.g., Hg_2^{2+}) or strongly complex it (e.g., Tl^{3+} , Hg^{2+} , Pd^{2+}) must be removed before the Ag^+ is titrated. Many substances (e.g., Cu^{2+}) complex thiocyanate rather

strongly, but not sufficiently to interfere at moderate concentrations. (4) Colored substances may interfere with establishing the end point. Cu^{2+} , Ni^{2+} , and Co^{2+} form colored complexes with thiocyanate, and give trouble at high concentrations; however, moderate concentrations are tolerable. (5) Coprecipitable substances such as sulfates may be tolerable at moderate concentrations, but may cause error at higher concentrations (A13).

PROCEDURE

1. Weigh out three separate samples of the alloy, placing each in a 250-ml Erlenmeyer flask. (Notes 1-3.) To each flask, add 10 ml of water and 10 ml of conc. HNO_3 . Heat the mixture until the alloy is dissolved. After solution is complete, make up to about 25 ml with water. Boil for a few minutes to remove NO_2 . Cool, and add water to about 70 ml.

2. Add 5 ml of 0.33 M $\text{Fe}(\text{NO}_3)_3$ as indicator. (Note 4.) Titrate to the first faint tinge of orange which persists on swirling vigorously for at least a half-minute. (Note 5.)

3. Determine a blank, using 100 ml of water, 5 ml of 1:1 HNO_3 (Note 2, Exp. 16.4), 5 ml of 0.33 M $\text{Fe}(\text{NO}_3)_3$, and enough 0.5 M $\text{Cu}(\text{NO}_3)_2$ solution to give to the blank a blue tint comparable to that of the sample solution. (Note 6.)

4. Calculate the % Ag in the alloy for each determination, and report the average. (Notes 7, 8.)

NOTES

(1) Metal samples need not be oven-dried; however, they should be free from grease and corrosion. If they are greasy, rinse them in reagent-grade benzene, blot with filter paper, and dry in air. If they are corroded, remove the corrosion layer by rubbing lightly with emery paper. Wipe off all loose particles of grit before weighing the samples.

(2) The sample size should be such as to require 35-45 ml of 0.1 M KSCN for titration. Unless samples are precut, the student should find the approximate Ag content from the instructor, so that the proper sample size may be chosen.

(3) Alloy samples are often nonuniform. Individual samples should be used, so that any large sampling errors may be revealed.

(4) Two milliliters of a saturated solution of ferric alum, $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$, are sometimes used. This does not give a sufficiently high sulfate concentration to cause error.

(5) The color is best observed in the supernate, after the precipitate is allowed to settle for a few seconds. If the sample contains enough copper to color the solution blue, the end point is the first sharply perceptible change from blue to greenish.

(6) The blank should require less than 0.02 ml of 0.1 M KSCN. This method of determining the blank is not suitable if the reagents contain chloride as an impurity, since such a blank would be negative.

(7) For excellent work, the relative range of three determinations should be about 0.2% or less.

(8) Pour all waste solutions and precipitates containing Ag into the jars marked "Silver Residues."

EXPERIMENT 16.4. THE VOLHARD DETERMINATION OF CHLORIDE

THEORY

The Volhard method may be used for the indirect determination of chloride. The chloride is precipitated by adding a measured excess of standard AgNO_3 . Then the AgCl is removed or inactivated, and the excess AgNO_3 is determined by titration with standard KSCN , Fe^{3+} being used as an indicator. The moles of Ag^+ reacting with the chloride (and therefore the moles of chloride in the sample) may be calculated by difference, as in the following example.

Example. To a 1.000-g sample containing NaCl and NaNO_3 , 50.00 ml of 0.1000 M AgNO_3 are added. The AgCl is filtered off and washed, the washings being added to the filtrate. Titration of the filtrate by the Volhard method requires 3.32 ml of 0.1060 M KSCN . Calculate the % Cl in the sample, assuming that blanks and end-point errors are negligible.

$$\begin{aligned} \left(\begin{array}{c} \text{mmoles Cl}^- \\ \text{in sample} \end{array} \right) &= \left(\begin{array}{c} \text{total mmoles} \\ \text{Ag}^+ \text{ added} \end{array} \right) - \left(\begin{array}{c} \text{excess mmoles Ag}^+ \\ \text{titrated by KSCN} \end{array} \right) \\ &= (0.1000 \times 50.00) - (0.1060 \times 3.32) = 4.648 \\ \% \text{ Cl in sample} &= 4.648 \times 35.453 \times \frac{1.000}{10.00} = 16.48\% \end{aligned}$$

For the back titration of the excess AgNO_3 with standard KSCN , the conditions and limitations of Exp. 16.3 hold. Also, interference due to AgCl in the back titration must be eliminated. AgCl is more soluble than AgSCN , and, if not removed, the AgCl would be metathesized to AgSCN before $[\text{SCN}^-]$ rises sufficiently high to give the end-point coloration.



This reaction would cause a fading end point and a low value for the Cl content of the sample. There are several ways of preventing this interference. (1) Remove the AgCl by filtration. Although excellent results may be obtained in this way, the slowness and chances of loss in the filtration are objectionable. (2) Inactivate the AgCl with an immiscible organic liquid, such as nitrobenzene. The rate of metathesis is thus reduced sufficiently to ensure a good end point. This is the technique used in this experiment. (3) Increase $[\text{Fe}^{3+}]$ sufficiently so that $[\text{SCN}^-]$ at the equivalence point is too low to metathesize AgCl . Such an increase is feasible, as indicated in Probs. S11 and S12 (p. 766).

Interferences. All anions in the first column of Table 16.3 form Ag salts insoluble in acid solution, and react in the same way as chloride. When such anions are present, only the total anion content may be obtained by the indirect Volhard method. If chloride alone is desired, such interfering anions must generally be removed before titration. However, chloride may sometimes be titrated in the presence of Br^- , I^- , etc. (p. 760).

Other applications. For the very reason that they interfere, the anions in the first column of Table 16.3 may be determined in the same way as chloride. In fact, those Ag salts (AgBr , AgI , AgSCN) that have approximately the same solubility as AgSCN (or lower) need not even be removed before the back titration. On the other hand, those anions whose Ag salts are only moderately insoluble (cyanate, iodate) may be determined by adding an excess of AgNO_3 to repress the solubility, and filtering off the precipitate before back titration. (See Prob. S4, p. 767.)

Theoretically, the anions in the second column of Table 16.3 are also determinable by precipitation with excess of standard AgNO_3 in solutions of low acidity. After the precipitate and filtrate are separated, (1) the excess Ag^+ in the filtrate may be determined by the Volhard method after acidification, or (2) the precipitate may be dissolved in acid solution and the Ag^+ determined by the Volhard method. $\text{AsO}_4^{=}$ and $\text{PO}_4^{=}$ are determined in this way at the 1% error level (K19). These procedures are not highly precise because of solubility losses in washing and variable composition of the precipitates.

Chlorine may be determined in organic compounds by procedures similar to those described in the Supplement (p. 735), except that the resulting chloride is titrated by the Volhard method instead of being determined gravimetrically.

PROCEDURE

1. Dry sample 2 hours at $105\text{--}110^\circ\text{C}$. To the nearest 0.1 mg, weigh out 1.1–1.3 g of sample and dilute to volume in the 250-ml volumetric flask. (Note 1.)

2. To a 50-ml aliquot of the sample solution in a 250-ml Erlenmeyer flask add 5 ml of 1:1 boiled HNO_3 . (Note 2.)

3. From a buret, add a measured excess of standard 0.1 M AgNO_3 , swirling the flask contents continually. (Note 3.) Continue swirling for a half-minute after adding the AgNO_3 , until the precipitate coagulates. Permit the precipitate to settle until a fairly clear supernate may be seen. Test for complete precipitation by adding one drop of standard AgNO_3 and looking for further precipitation. This drop must be included in the volume of standard AgNO_3 added. Add 4 ml of nitro-

benzene, stopper the flask with a clean rubber stopper, and shake vigorously for about a minute, until all AgCl is coated with nitrobenzene, and the supernate is clear.

4. Add 5 ml of 0.33 M $\text{Fe}(\text{NO}_3)_3$ indicator solution, and back-titrate with standard KSCN , as in step 2, page 300.

5. Perform the titration in triplicate, and calculate the average volume of standard AgNO_3 required to react with a 50-ml aliquot of sample solution. (Notes 4-6.)

6. From the average volume of AgNO_3 equivalent to a 50-ml sample aliquot, calculate and report the % Cl in the sample.

NOTES

(1) Pure NaCl-KCl mixtures are recommended as unknowns in this experiment. See Note 1, page 297, for selection of sample size.

(2) Dilute 15 ml of conc. HNO_3 with 15 ml of water, and boil for a few minutes to remove NO_2 . Cool before using.

(3) For a good determination, an excess no greater than 1 ml should be used. To determine the proper amount, carry out a preliminary titration on a 25-ml aliquot, without concern for keeping the excess small, and calculate the approximate volume of standard AgNO_3 equivalent to a 50-ml aliquot. On subsequent accurate determinations of 50-ml aliquots, add this volume of standard AgNO_3 plus 0.5 ml. In the presence of nitrobenzene, etc., the AgSCN precipitate formed is not very pure, and the back titration is not very accurate. The excess of Ag is kept small to minimize the error.

(4) The blank is troublesome to determine properly. Since it is small (0.01-0.02 ml), it is better to disregard it than to chance applying it improperly.

(5) The Cl content could be calculated according to the example on page 301, but for the replicate determinations of this experiment it is simpler first to find the volume of standard AgNO_3 equivalent to the chloride in the sample, and then to calculate the Cl content from this.

$$\left(\begin{array}{c} \text{ml AgNO}_3 \\ \text{equivalent to the} \\ \text{sample aliquot} \end{array} \right) = \left(\begin{array}{c} \text{total ml} \\ \text{AgNO}_3 \\ \text{added} \end{array} \right) - \left(\begin{array}{c} \text{ml AgNO}_3 \text{ equivalent} \\ \text{to ml KSCN used} \\ \text{in back titration} \end{array} \right)$$

The last term may be calculated by multiplying the volume of KSCN by the ratio of the concentrations of KSCN and AgNO_3 .

(6) For excellent work, the range of triplicate determinations should be less than 0.2%.

EXPERIMENT 16.5. THE MOHR DETERMINATION OF CHLORIDE

THEORY

The action of chromate as an indicator in the Mohr titration of chloride is described on page 281. Although the limitations of the Mohr method make it generally inferior to the Fajans and Volhard methods, it is an instructive example of a titer method in which the end-point

error in the sample titration is compensated by that in standardization. For accurate performance of the Mohr titration, an understanding of the following facts is necessary.

End-point error and indicator concentration. The $[\text{CrO}_4^{2-}]$ should be about 0.002 *M*. If $[\text{CrO}_4^{2-}]$ is much higher than this, the yellow color interferes with the end point, whereas if it is much lower, the end-point coloration is faint and may not appear until well past the equivalence point. The illustrative examples on page 282 indicate that the end-point error is about 0.04 ml. In this calculation, however, two facts are ignored, both of which make the observed error larger than the calculated one, and neither of which is calculable. (1) Some of the Ag_2CrO_4 must actually be formed to be perceptible. The amount required depends on the individual worker, and also upon the size of the sample, since the AgCl masks the color of the Ag_2CrO_4 to some extent. (2) Since an excess of Ag^+ must be built up to reach the end point, there is opportunity for Ag^+ to be adsorbed on the AgCl .

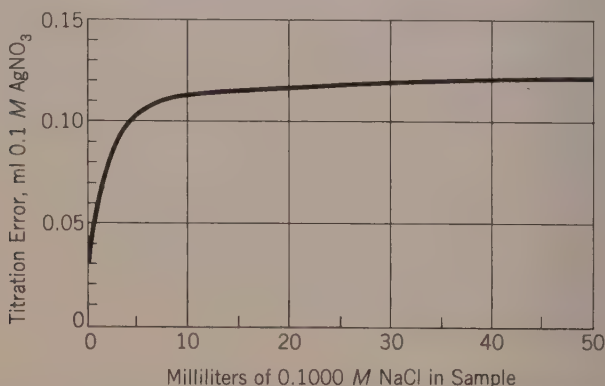
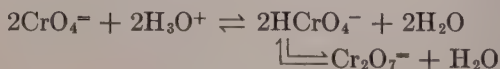


FIG. 16.7. End-Point Error in the Mohr Titration—End-point conditions: volume, 100 ml; K_2CrO_4 concentration, 0.002 *M*.

The dependence of end-point error upon sample size is shown in Fig. 16.7, which was obtained experimentally by measuring the volume of 0.1000 *M* AgNO_3 required to titrate precisely measured portions of 0.1000 *M* NaCl .

The end-point error is substantial, and may be corrected for by the methods described generally on pages 49–51. The following have been used for the Mohr method. (1) Determine a blank on a sample of distilled water. Inspection of Fig. 16.7 shows this procedure to be highly inadequate. Such a blank would be 0.03 ml, whereas the end-point error for most samples would be around 0.12 ml. (2) Use sample sizes above 10 ml of 0.1 *M* NaCl , in which case the end-point error is virtually con-

Acidity. The Mohr titration must be performed between pH 6 and 10. If the basicity becomes too high, some of the standard AgNO_3 forms brownish AgOH . If the acidity is too high, an appreciable proportion of the chromate is converted to dichromate, and the end point comes too late. If the solution is highly acid, no end point will be observed at all.



Temperature and ionic strength. In order that it may be properly corrected for, the end-point error must be reproducible. The magnitude of the error depends upon the solubilities of AgCl and Ag_2CrO_4 , and these in turn depend upon temperature and ionic strength. The titer value of the standard solution should be determined at a temperature within a few degrees of that at which the unknown sample is titrated, and in a solution similar in composition to that of the unknown sample.

Stirring. Good stirring during the entire addition of AgNO_3 is most important in the Mohr method. With poor stirring, Ag_2CrO_4 forms locally before the equivalence point and becomes occluded by subsequently formed AgCl , giving an end point that is neither sharp nor reproducible.

Interferences. Since the Mohr titration is performed in neutral solution, interferences are practically identical with those of the Fajans method. However, some anionic interferences are reported to be not so severe as solubility considerations might indicate (B7). Samuelson describes the removal of interferences by ion exchange (S1).

Other applications. Because of the many interferences and limitations, the Mohr method is not widely applicable. For example, it might be supposed that chromate could be used as an indicator in the direct titration of AgNO_3 with standard NaCl , the end point being the disappearance of the Ag_2CrO_4 coloration. But when it is formed in a large excess of AgNO_3 , Ag_2CrO_4 becomes compacted and occluded by subsequently precipitated AgCl . The Ag_2CrO_4 does not dissolve readily as the end point is approached, and the titration is impractical. To determine Ag by the Mohr method, a back-titration procedure must be used. A measured excess of standard NaCl is added to the unknown AgNO_3 solution, then K_2CrO_4 indicator is added, and finally the excess NaCl is titrated with standard AgNO_3 solution.

It might also be supposed that anions forming Ag salts more insoluble than AgCl (Table 16.3, p. 296) could be determined by direct titration with standard AgNO_3 and K_2CrO_4 indicator, but this is not the case. The colors of most of the Ag salts interfere; only AgSCN , AgCN , and

AgIO_3 are white. AgIO_3 is too soluble for accurate determination. In the titration of thiocyanate and of iodide, adsorption of the negative ion on the precipitate is not readily reversible, and desorption is slow as the equivalence point is approached. Of all the anions listed in Table 16.3, only bromide and cyanide may be determined by direct titration. For all these anions, other titration methods exist that are more precise and convenient than the Mohr titration.

PROCEDURE

1. Dry the sample 2 hours at $105\text{--}110^\circ\text{C}$. To the nearest 0.1 mg, weigh 1.30–1.32 g into a small beaker, transfer to the 250-ml volumetric flask, and dilute to volume. (Note 1.)

2. Pipet a 50-ml aliquot of the sample solution into a 250-ml Erlenmeyer flask, add 2.0 ml of 0.10 M K_2CrO_4 indicator solution, and titrate with standard AgNO_3 . (Notes 2–4.)

3. Perform triplicate titrations of the sample solution, and calculate the average volume of AgNO_3 required per 50-ml aliquot of sample solution. (Note 5.)

4. Determine the titer value of the AgNO_3 solution. (a) Dry 1.3–1.5 g of reagent-grade NaCl in a small weighing bottle at $105\text{--}110^\circ\text{C}$ for 2 hours. (b) To the nearest 0.1 mg, weigh 1.16–1.18 g into a small beaker, transfer to the 250-ml volumetric flask, and dilute to volume. (Note 6.) (c) Titrate triplicate 50-ml aliquots of the standard NaCl solution as in step 2. (Note 5.) (d) Calculate the chloride titer of the AgNO_3 solution. (Note 7.)

5. Calculate the % Cl in the unknown sample.

NOTES

(1) The samples are NaCl-KCl mixtures. It should be shown that 35–45 ml of 0.1 M AgNO_3 are required to titrate a 50-ml portion of the sample solution, no matter what the percentage composition of the sample. The range of sample size is restricted so that the titer method will give accurate results. If samples of different composition are used, the instructor will announce the proper sample size.

(2) The unknowns of the elementary course are neutral, and the acidity need not be adjusted. If neutralization is necessary, see Note 2, page 297.

(3) The end point is the first sharply perceptible appearance of orange that persists on swirling the solution vigorously. Setting the flask on a sheet of white paper aids in detecting the color change.

(4) Standard AgNO_3 is not necessary, since the titer value must be determined anyway. However, it is instructive to use standard AgNO_3 if it is available, since the magnitude of the end-point error may then be found.

(5) The relative range of triplicate titrations should be less than 0.2% for excellent work.

(6) A 50-ml aliquot of the NaCl solution should require about 40 ml of the AgNO_3 for titration; thus the volume of AgNO_3 used in titrating unknown samples (35–45

ml) will always be within 5 ml of the volume used in standardization. Considerations similar to those of the example on page 305 show that compensation of errors by the titer method is very good, and that residual errors will be less than 0.05%, relative. The weight of NaCl required for 250 ml of solution is

$$0.1000 \times 40 \times \frac{250}{50} \times \frac{58.44}{1000} = 1.17 \text{ g}$$

mmoles NaCl for 250 ml of solution

mmoles AgNO_3 in 40 ml of 0.1 *M* solution,* or mmoles NaCl required in 50-ml aliquot

The procedure of this experiment is suitable only for a rather narrow range of sample compositions. If the sample composition varies widely, and if several different samples must be titrated, adjustment of the sample size becomes onerous. In such cases, the superiority of determining the end-point error and applying it as a correction should be apparent.

(7) This is the weight of chloride per 50-ml aliquot of NaCl solution divided by the average volume of AgNO_3 required for titration.

QUESTIONS

Section 16A

1. Explain qualitatively why the sought-for ion concentration changes greatly as titrant is added near the equivalence point.
2. Explain why all the curves of Fig. 16.4 (p. 279) approach the same limit after the equivalence point.
3. On Fig. 16.4, sketch roughly the curve for pX , when $K_s = 1.0 \times 10^{-12}$.
4. A 100.00-ml portion of 0.1000 *M* AgNO_3 is titrated with 0.1000 *M* NaCl. Draw a rough titration curve showing pAg . Make no precise calculations, but indicate pAg and volume of NaCl at the equivalence point. Label this reference curve *R*. Draw this curve in quadruplicate, using one plot for each part of this question. (a) On one of the plots show what the curve would look like if the titration were performed at 90°C. Label this curve *A*, and draw it so that it may be compared to curve *R*. (b) On a second plot show what the curve would look like if the AgNO_3 were diluted to 500 ml before titration. Label this curve *B*, and draw it so that it may be compared to curve *R*. (c) On a third plot show comparatively what the curve would look like if 0.1000 *M* NaI were used instead of NaCl. (d) On the fourth plot show comparatively what the curve would look like if 0.01000 *M* solutions were used instead of 0.1000 *M*.
5. Explain carefully what is meant by saying that the curve for the titration of NaCl with AgNO_3 is symmetrical about the equivalence point. Using the solubility-product expression for Ag_2CrO_4 , explain why the curve for the titration of K_2CrO_4 with AgNO_3 is unsymmetrical about the equivalence point.

Section 16B

1. In the gravimetric determination of chloride as AgCl , solubility of the AgCl causes loss and systematic error. Describe and classify the error caused by solubility in the volumetric determination of chloride as AgCl .

*If the ratio of weights of standard NaCl and of unknown sample is always kept close to 1.17/1.31, each will require about the same amount of standard AgNO_3 for titration, regardless of the AgNO_3 concentration. Sample sizes need not be adjusted to the concentration of the standard AgNO_3 solution. However, the AgNO_3 concentration should lie between 0.09 and 0.11 *M*; otherwise the volumes required for titration of the recommended samples may lie outside the 30–50 ml range.

2. For which of the substances in Fig. 16.4 would it be most difficult to select an indicator that would give an end point within a few tenths of a per cent of the equivalence point? What would be the practical difficulties of using such an indicator?

3. What is meant by saying that in the titration of NaCl with AgNO_3 the proportion of the added AgNO_3 precipitated in each successive drop decreases through the region of the equivalence point?

4. In the determination of Cl by the method of equal turbidity, the turbidity produced in the portion to which AgNO_3 is added is greater than the turbidity in the portion to which NaCl is added. Is the titrated solution before or beyond the equivalence point?

5. It is desired to determine sulfate in 0.1 M solution by titration with standard 0.1 M $\text{Pb}(\text{NO}_3)_2$. Explain why K_2CrO_4 cannot be used as an external indicator.

Section 16C

1. Explain why there is always a tendency for coprecipitation of the reagent or sought-for substances in a precipitation titration. Give examples, and specify the signs of the errors.

2. Give an example of coprecipitation that would cause error in a gravimetric analysis, but not in a volumetric analysis based on the same reaction.

3. Suppose that the rate of precipitation is too low in a titration. What might be done to overcome this difficulty?

4. The direct titration of KIO_3 with AgNO_3 lacks a sharp end point because AgIO_3 is only moderately insoluble. What might be done to increase the sharpness of the end point?

Experiment 16.1

1. None of the primary standard substances NaCl, KCl, KBr, KSCN, or AgNO_3 forms very stable hydrates. Considering the stringent means required to remove the last traces of water, specify by what mechanism it must be held.

2. Criticize or defend the following statement: "If a student obtains poor precision in standardizing his solution, he will probably obtain poor accuracy in titration of his unknown." Repeat the criticism or defense with "good" substituted for "poor."

Experiment 16.2 (the Fajans method)

1. Contrast the relative merits of using aliquots of a single sample (as in Exp. 16.2) with using individual samples for each determination (as in Exp. 16.3).

2. How might the end-point error be determined? Why can a blank not be determined?

3. In the preparation of the standard AgNO_3 and KSCN solutions, would the check of Exp. 16.1 reveal any error in the volumetric flask calibration? Describe the error, if any, caused by such a faulty calibration on the Cl content of a sample as determined in Exp. 16.2.

4. In testing a particular adsorption indicator (HX) for a particular titration, it is found that the end point comes a little too far past the equivalence point. What measures might be used to decrease this end-point error?

5. Instead of decreasing the pH to reduce the error when dichlorofluorescein is used in the $\text{Ag}^+\text{-Cl}^-$ titration, why not simply decrease the indicator concentration?

6. Give the effect of each of the following mistakes in Exp. 16.2, assuming that no others are made. If determinate, give the sign of the error. (a) The water used to

dissolve the sample contains appreciable chloride. (b) The weight of a 1.1011-g sample is incorrectly recorded as 1.1101 g. (c) Aliquots for titration are withdrawn before the contents of the volumetric flask are mixed. (d) Dextrin is omitted. (e) The volume of AgNO_3 is erroneously recorded as 38.92 ml instead of correctly as 38.42 ml.

7. Considering that adsorbed dichlorofluoresceinate gives the same color as silver dichlorofluoresceinate, is it correct to say that dichlorofluoresceinate is in the counter-ion layer?

8. A solution contains $10^{-3} M$ NaCl , $10^{-5} M$ dichlorofluorescein, and a little dextrin. On slowly adding $1 M$ AgNO_3 , the precipitate first formed is white, then changes sharply to red, and finally becomes almost white again in excess AgNO_3 . Explain these color changes in terms of adsorption phenomena.

Experiment 16.3 (the Volhard method for Ag)

1. Why is HNO_3 used to dissolve the alloy, rather than H_2SO_4 ?
2. Give the effect of each of the following mistakes in Exp. 16.3, assuming that no others are made. If determinate, give the sign of the error. (a) The blank is not determined. (b) The sample solution is not cooled before titration. (c) Such a sample size is taken that only 5.82 ml of KSCN are required for titration.
3. How would the presence of appreciable Cl^- in the distilled water be revealed? Would the value of the blank be affected by Cl^- in the distilled water?

Experiment 16.4 (the Volhard method for Cl)

1. How may NO_2 be formed in conc. HNO_3 ?
2. Speculate as to the nature of the error if nitrobenzene and indicator are added with the HNO_3 in step 2.
3. Explain the nature of the error if the excess of AgNO_3 is not kept low.
4. If thiocyanate is to be determined by the Volhard method, it must be determined indirectly, in a manner similar to that for chloride. Speculate as to why the direct titration to the disappearance of the red coloration is inaccurate.
5. Explain why AgCN is only moderately insoluble in acid solution, even though the solubility product is very low. Outline a procedure for the determination of NaCN by the Volhard method.
6. If a fading end point is noted in Exp. 16.4, what might be the remedy?
7. What is the nature of the error if the water used to dissolve the sample contains chloride?

Experiment 16.5 (the Mohr method)

1. The Mohr method tolerates up to $0.01 M$ K_2SO_4 at the end point without appreciable coprecipitation error. Explain how to analyze a solution containing about (a) $0.1 M$ KCl and $0.03 M$ K_2SO_4 , (b) $0.1 M$ KCl and $1.0 M$ K_2SO_4 .
2. Write equations to show how NH_4^+ interferes in the Mohr titration at high pH. Explain how to analyze for chloride by the Mohr method in a solution containing about $0.1 M$ NH_4Cl and $0.1 M$ NH_4NO_3 .
3. Explain what is wrong or inadequate about the following statement: Most cation interferences in the Mohr method may be easily removed by a single precipitation of the hydroxides.
4. Speculate on the nature of the errors that might explain the shape of the curve in Fig. 16.7 (p. 304).
5. An AgNO_3 solution is standardized by the Mohr and Fajans titrations against

primary standard NaCl. No corrections for end-point error are made. How do the concentrations of AgNO_3 calculated by each method compare?

6. Prepare a table similar to that on page 202, comparing the Fajans, Volhard, and Mohr methods for chloride.

7. In the Mohr method for chloride, the blank is sometimes determined on a suspension of chloride-free CaCO_3 . Discuss the possible shortcomings of this procedure.

PROBLEMS

Sections 16A, B

1. Show that a change of 1.44 $p\text{Ag}$ units corresponds to a 28-fold change in $[\text{Ag}^+]$.
 2. Verify the data of Table 16.1 (p. 276) for the following points in the titration: 40.00, 49.90, 50.00, 50.05, 51.00 ml of AgNO_3 .

3. Calculate the change in $p\text{Ag}$ for the titration of 50.00 ml of 0.1000 M NaBr with 0.1000 M AgNO_3 , in going from 49.95 to 50.05 ml of AgNO_3 . Compare this with the corresponding change for the NaCl- AgNO_3 titration of Table 16.1.

Ans. 3.71 units.

4. For the conditions of Fig. 16.3 (p. 278), calculate $p\text{Ag}$ when 50.50 ml of AgNO_3 are added, the equivalence-point volume being 800 ml. Verify the answer with the plot.

5. Calculate $p\text{Ag}$ when 47.00, 49.00, and 49.50 ml of 0.01000 M AgNO_3 are added to 50.00 ml of 0.01000 M NaCl. Use these points to plot the curve for the titration of 0.01 M solutions onto Fig. 16.2 (p. 277). (Assume K_s for AgCl is 1.00×10^{-10} .)

Ans. $p\text{Ag} = 6.00$ at 49.00 ml.

6. For titration curves like Figs. 16.1 to 16.4, it is sometimes desirable to express the amount of standard reagent added as a percentage of the equivalent amount, rather than as the number of milliliters. Draw a second axis of abscissae onto Fig. 16.2, with the origin at the 50-ml point. Let distance to the right of the origin represent % excess AgNO_3 , and distances to the left % excess NaCl. Explain how this scale of abscissae is useful in discussing titration errors.

7. Show that $p\text{Ag} + p\text{Cl} = pK_s$, starting with the solubility-product expression. Use this relationship to sketch the $p\text{Cl}$ curve for 800 ml into Fig. 16.3.

8. A 50.00-ml portion of 0.1000 M NaCl is titrated with 0.0600 M AgNO_3 . Calculate $p\text{Ag}$ and $p\text{Cl}$ when the following volumes of AgNO_3 have been added: 60.00, 61.50, 62.00, 62.25, 62.40, and 62.50 ml. Draw the titration curves.

9. In the titration of Zn^{2+} with $\text{Fe}(\text{CN})_6^{4-}$ and an external indicator, calculate the relative error if 0.3 ml of the titrated solution is withdrawn 2% before the equivalence point to perform the spot test, and if the result is not corrected for this withdrawal. Assume that the titration volume is about 100 ml.

Ans. 0.006%.

10. Under the titration conditions of Fig. 16.4 (p. 279), within what $p\text{Ag}$ range must an indicator change in order to locate the equivalence point within 0.3% error, if the precipitate formed has a solubility product of 10^{-6} ? Explain why use of such an indicator would not be accurate, even if one could be found.

11. The titration curves of Figs. 16.2 to 16.4 are symmetrical because the volume of the titrated solution changes insignificantly over the narrow range that is shown. For the conditions of Table 16.1, calculate $p\text{Ag}$ and $p\text{Cl}$ when 100.00 ml of 0.1000 M AgNO_3 have been added, and show that the titration curve is perceptibly unsymmetrical over a wide range about the equivalence point. (The lack of symmetry is caused by dilution. Were the titration performed at constant volume, the curve would be symmetrical.)

12. In the illustrative example on page 277, calculate $p\text{Ag}$ when 0.10 ml less than the equivalent volume of 0.1000 M AgNO_3 is added.

13. Calculate $p\text{Ag}$ and $p\text{CrO}_4$ when 25.00 ml of 0.1750 M AgNO_3 are added to 19.00 ml of 0.0950 M K_2CrO_4 . *Ans.* $p\text{Ag} = 1.76$; $p\text{CrO}_4 = 8.37$.

14. A 50.00-ml portion of 0.1000 M KI is titrated with 0.1000 M AgNO_3 . (a) Calculate the concentration of Ag^+ at the equivalence point. (b) Draw an approximate titration curve for this titration, plotting $p\text{Ag}$ against ml AgNO_3 added. Label the coordinates and indicate the equivalence point. (c) Superimpose on the plot of part a the curve that you would expect if both solutions were 0.01 M . Label both curves distinctly. (d) An indicator is used for the titration of the 0.1 M solutions, and this indicator changes at $p\text{Ag}$ 4.00. What is the end-point error, expressed as milliliters of 0.1 M AgNO_3 ?

15. A 47.00-ml portion of 0.1327 M AgNO_3 is titrated with standard 0.0875 M K_2CrO_4 . (a) What is the volume of K_2CrO_4 required to reach the equivalence point? (b) What is the silver-ion concentration at the equivalence point? (c) If the titration is carried to an end point at which $[\text{Ag}^+]$ is $0.8 \times 10^{-4} M$, what is the end-point error—that is, what volume of standard K_2CrO_4 must be added past the equivalence point to reach this end point?

Ans. (a) 35.64 ml; (b) $1.37 \times 10^{-4} M$; (c) 0.15 ml.

16. A 50.00-ml portion of 0.1000 M NaCl containing 0.0020 M K_2CrO_4 is titrated with 0.2000 M AgNO_3 . Calculate the end-point error.

17. An NaCl sample is titrated with standard 0.1000 M AgNO_3 . A precipitation indicator Ag_3B ($K_s = 1.00 \times 10^{-17}$) is to be used. What molar concentration of indicator ion ($\text{B}^{=}$) should be selected so that the indicator precipitate will just begin to form at the equivalence point? *Ans.* 0.0042 M .

18. In the titration of 0.1000 M NaBr with 0.1000 M AgNO_3 , what $[\text{CrO}_4^{=}]$ would have to be present in order to form Ag_2CrO_4 at the equivalence point? What would be a good concentration of chromate to use?

19. Calculate the end-point error in the Mohr titration of 50.00 ml of 0.1000 M NaCl with 0.1000 M AgNO_3 at 70°C . The K_2CrO_4 concentration is 0.0020 M at the end point. The solubility of Ag_2CrO_4 at 70°C is 80 mg/l, and that of AgCl may be estimated as 9.5 mg/l from Fig. 11.1 (p. 162). How would the sharpness of the end point compare with that at 25°C ? *Ans.* 0.14 ml of 0.1 M AgNO_3 ; less sharp.

20. From solubility considerations alone, what $[\text{IO}_3^-]$ could be present at the end point without interference in the Mohr titration of 50.00 ml of 0.1000 M NaCl with 0.1000 M AgNO_3 , with $[\text{CrO}_4^{=}]$ equal to 0.0020 M ? Why is it improper to assume that this "tolerable" $[\text{IO}_3^-]$ (or even a considerably smaller concentration) would not interfere?

21. In Ex. 2, page 282, a student reasons that the end-point error is equal to the volume of 0.1000 M AgNO_3 that must be added to 100 ml of 0.002 M K_2CrO_4 in order just to saturate the solution with respect to Ag_2CrO_4 . Calculate this volume, compare the answer with that of Ex. 2, and explain the fallacy of the reasoning.

Ans. 0.025 ml.

22. What is the upper limit to the $p\text{H}$ in the titration of 50.00 ml of 0.1000 M NaCl with 0.1000 M AgNO_3 , in order that no AgOH will precipitate up to the chloride equivalence point? For some methods like the conductometric, the equivalence point must be passed. What is the upper $p\text{H}$ limit in order that no AgOH will precipitate when the equivalence point has been exceeded by 10.00 ml of AgNO_3 ?

23. After the manner of Ex. 1, page 285, calculate the end-point error if $[\text{Fe}^{3+}]$ is only 0.001 M at the equivalence point.

Ans. 0.012 ml past eq. pt., or 0.024%, relative.

24. A 0.900-g portion of a Zn ore is dissolved and interferences are separated. If 34.58 ml of standard $\text{K}_4\text{Fe}(\text{CN})_6$ are required for titration, calculate the Zn content of the ore as % ZnCO_3 . The standard solution is prepared by dissolving 4.752 g of pure $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ in water and making up to volume in a 500-ml volumetric flask. (What would be a better way to standardize the ferrocyanide solution?)

Experiment 16.1

1. How much AgNO_3 is required to prepare 500 ml of 0.100 *M* solution?

Ans. 8.5 g.

2. What is the molarity of a KSCN solution made by dissolving 4.880 g KSCN to give 500.23 ml of solution at 28°C? What is the molarity of the solution at 20°C?

3. What range of weights of KSCN may be taken to prepare 500.0 ml of 0.10000 \pm 0.00005 *M* solution?

Ans. 4.857–4.861 g.

4. What is the molarity of a KSCN solution if 50.00 ml require 42.85 ml of 0.0985 *M* AgNO_3 for titration?

5. What volume of 0.972 *M* KSCN is required to titrate a 25.00-ml aliquot of 0.921 *M* AgNO_3 solution?

Ans. 23.69 ml.

Experiment 16.2 (the Fajans method)

1. What is the percentage of chloride in an NaCl-KCl sample, 0.3000 g of which requires 48.72 ml of 0.0989 *M* AgNO_3 for titration?

Ans. 56.9%.

2. A 1.000-g sample of an NaCl-KCl mixture is diluted to 250 ml. Titration of four 50.00-ml aliquots requires 38.33, 38.28, 38.21, and 38.12 ml of 0.1108 *M* AgNO_3 . Report the % Cl in the sample.

3. What volume of 0.0987 *M* AgNO_3 is required to titrate a 0.2046-g sample of pure NaCl?

Ans. 35.47 ml.

4. Compute roughly the molar concentration of dichlorofluorescein indicator at the end point in Exp. 16.2.

5. A sample may contain only BaCl_2 and NaCl, but in any proportion. What range of sample sizes may be taken so that 25–50 ml of 0.100 *M* AgNO_3 are required for titration?

Ans. 0.26–0.29 g.

6. Is Prob. 5 solvable if it is desired to make the volume range 40–50 ml? Explain.

7. It is desired to find the volume of a large, stationary, irregular tank, and metering equipment is not available for measuring the amount of water required to fill the tank. A 500.0-g sample of primary standard NaCl is flushed quantitatively into the tank, which is then filled with distilled water. After thorough mixing of the contents, a 50.0-ml aliquot of the tank contents requires 3.13 ml of 0.1500 *M* AgNO_3 for titration. What is the volume of the tank?

Ans. 912 l.

8. Repeat the computation of Prob. 7 if tap water with a Cl content of 42 p.p.m. is used to fill the tank instead of distilled water.

Experiment 16.3 (the Volhard method for Ag)

1. An Ag-Cu alloy contains 60–70% Ag. What range of sample sizes may be taken, so that 30–50 ml of 0.100 *M* KSCN are required for titration?

Ans. 0.54–0.77 g.

2. A 1.053-g sample of an Ag-Cu alloy requires for titration 38.26 ml of 0.0903 *M* KSCN. What is the % Ag in the alloy?

3. A 0.1967-g sample of pure, electrolytic Ag requires for titration 21.37 ml of a KSCN solution. Compute the Ag titer and molarity of the KSCN.

Ans. 9.205 mg/ml; 0.08533 *M*.

4. What volume of 0.0909 M KSCN is required to titrate a 0.1700-g sample of AgNO_3 ?

5. An aqueous solution contains HNO_3 and AgNO_3 as the only solutes. A 25.00-ml portion of the solution requires 27.52 ml of 0.1192 M NaOH for titration, and another 50.00-ml aliquot requires 39.89 ml of 0.1000 M KSCN for titration. Give the composition of the original solution.

Ans. 0.1312 M HNO_3 , 0.0798 M AgNO_3 .

6. Hg^{2+} forms a very slightly dissociated, soluble complex, $\text{Hg}(\text{SCN})_2$, and may be determined by a procedure similar to the Volhard method for Ag. What is the molar concentration of $\text{Hg}(\text{NO}_3)_2$ in an aqueous solution, 50.00 ml of which require 48.90 ml of standard KSCN for titration? A 25.00-ml portion of the KSCN is equivalent to 33.85 ml of 0.1000 M AgNO_3 .

7. In a large school, about 350 students per year take elementary quantitative analysis. If each student prepares 500 ml of 0.100 M AgNO_3 , and the waste Ag is not recovered, how much Ag is lost? How much would this silver be worth purified, at \$16/ounce (avoir.)?

Ans. 67 ounces; \$1070.

Experiment 16.4 (the Volhard method for Cl)

1. A 47.25-ml portion of 0.1005 M AgNO_3 is added to a 0.2802-g sample of a NaCl-KCl mixture. The AgCl is inactivated with nitrobenzene, and 0.85 ml KSCN is used to back-titrate the excess AgNO_3 . 28.27 ml of the KSCN are equivalent to 25.98 ml of the standard AgNO_3 . Calculate the % Cl in the sample.

Ans. 59.1%.

2. A 1.2250-g sample of an NaCl-KCl mixture is diluted to 250.2 ml in a volumetric flask. After 42.23 ml of 0.0988 M AgNO_3 are added to a 50.00-ml aliquot of the sample solution, the AgCl is filtered off and washed quantitatively, and the washings are added to the filtrate. Back titration of the filtrate requires 2.06 ml of 0.1002 M KSCN. Calculate the % Cl in the sample.

3. To a 0.4481-g sample of an NaCl-KCl mixture in a 100.0-ml volumetric flask are added 20 ml of water and 75.00 ml of 0.1000 M AgNO_3 . The mixture is diluted to volume, shaken, and allowed to settle. Back titration of a 50.00-ml aliquot of the clear supernate requires 1.96 ml of 0.1005 M KSCN. Compute the % Cl in the sample.

Ans. 56.2%.

4. Bi may be quantitatively precipitated as BiOCl , which separates it from many other metals (§35). After such a procedure, the BiOCl is dissolved in HNO_3 , 25.00 ml of 0.1000 M AgNO_3 are added, the AgCl is inactivated with nitrobenzene, and 2.00 ml of 0.1006 M KSCN are used in the back titration. Compute the weight of Bi (as Bi_2O_3) present in the original sample.

Experiment 16.5 (the Mohr method)

1. What is the % Cl in a 0.3891-g sample that requires for titration 27.42 ml of an AgNO_3 solution whose Cl titer is 3.847 mg/ml?

Ans. 27.11%.

2. A 0.3538-g sample of primary standard NaCl requires 48.37 ml of an AgNO_3 solution for titration. Calculate the NaCl and Cl titers of the AgNO_3 . What is the BaCl_2 titer?

3. How many milligrams per milliliter of AgNO_3 are required to give a Cl titer of two mg/ml?

Ans. 9.583 mg/ml.

4. If the NaCl titer of an AgNO_3 solution is 5.972 mg/ml, what is the % Cl in a 0.2158-g sample that requires 31.47 ml of the AgNO_3 solution for titration?

5. Compute the following titers of a 0.1000 M AgNO_3 solution: Cl , NaCl , KClO_3 (after reduction to chloride). *Ans.* 12.26 mg KClO_3 /ml.

6. In the illustrative example on page 305, 15.00 ml of the AgNO_3 are required for titration of the sample, not 25.00 ml. Calculate the % Cl in the sample by the titer method. What is the relative error of this value?

7. In the example on page 305, what range of volumes of AgNO_3 must a sample require, in order that the relative error of its chloride content (as calculated by the titer method) will fall within 0.05%? *Ans.* 41–63 ml.

17 ACID-BASE EQUILIBRIA

It is the purpose of this chapter to familiarize the student with the acid-base equilibria encountered in titration systems. The dissociation of weak acids and bases is quantitatively described, and typical calculations are performed.

17A. IONIZATION OF ACIDS AND BASES

The ionization constant (K_i) is the equilibrium constant for the ionization of a weak electrolyte. The properties of K_i are described in an elementary way in Sec. 4C.3 (p. 26). As with other equilibrium constants, K_i for a particular solute is dependent upon (1) the nature of the solvent, (2) temperature, and (3) ionic strength. In addition, K_i has meaning only for the class of weak electrolytes (see Table 4.1, p. 22).

It must be kept in mind that the ionization reaction represents a reaction with the solvent. Thus, a weak acid (HA) ionizes in water because the water competes with A^- for the proton:



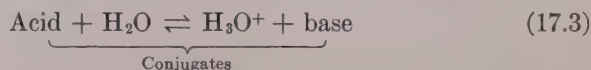
Likewise, the ionization of a base (B) gives hydroxyl ions by reaction with water:



*The anion A^- is also hydrated, but the degree of hydration is poorly known. Equations are therefore generally written with the hydration of anions implied, but not designated. The same remarks apply to the hydration of cations other than the proton.

This concept of acid and base ionization is due to Brönsted, and is fundamentally different from the classical theory** which regards the ionization as a simple splitting process.

According to Brönsted theory, when an acid (HA) loses its proton as in Eq. 17.1, a base (A^-) is formed. HA and A^- are called a *conjugate pair*: A^- is the conjugate base of the acid HA, and vice versa.

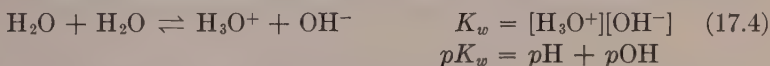


If the acid is a strong one, Eq. 17.3 lies far to the right, and the reverse reaction is slight; therefore, by definition, the conjugate base is a weak one. Likewise, a strong base has a weak conjugate acid. The strengths of acids and bases are described by their ionization constants (Secs. 17C, D).

It should be noted that acid and base species may be positively or negatively charged, or neutral. Examples of acids (i.e., proton donors) are NH_4^+ , HAc, and HPO_4^- . Examples of bases (i.e., proton acceptors) are OH^- , NH_3 , and $\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+$.

17B. IONIZATION OF WATER

Water is a very weak electrolyte. It is *amphiprotic*, which means that it can act either as an acid or as a base. The ionization reaction is



The dissociation is highly endothermic, and K_w increases rapidly with temperature, as shown in Table 17.1. This equilibrium exists in any aqueous solution, no matter what other solutes are present. Any solution, therefore, no matter how basic (or acidic), contains some H_3O^+ (or

TABLE 17.1
DEPENDENCE OF K_w^* ON TEMPERATURE

Temperature (°C)...	0	10	20	25	30	40	60	80	100
$K_w (\times 10^{14})$	0.115	0.293	0.681	1.01	1.47	2.92	9.61	23.4	51.3
pK_w	14.94	14.53	14.17	14.00	13.83	13.54	13.02	12.63	12.29

* Activity product.

**The simplicity of the classical theory is enticing, and it suffices for simple acids and bases in water. Recently, analysts have become interested in the behavior of amphiprotic organic substances and in nonaqueous acid-base titrations. These can be described better by Brönsted theory than by the classical theory.

TABLE 17.2

RELATIONSHIPS AMONG $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH , AND pOH IN DILUTE AQUEOUS SOLUTION AT 25°C

$[\text{H}_3\text{O}^+]$	pH	pOH	$[\text{OH}^-]$
1.0×10^1	-1	15	1.0×10^{-15}
10^0	0	14	10^{-14}
10^{-1}	1	13	10^{-13}
10^{-2}	2	12	10^{-12}
10^{-3}	3	11	10^{-11}
10^{-4}	4	10	10^{-10}
10^{-5}	5	9	10^{-9}
10^{-6}	6	8	10^{-8}
10^{-7}	7	7	10^{-7}
10^{-8}	8	6	10^{-6}
10^{-9}	9	5	10^{-5}
10^{-10}	10	4	10^{-4}
10^{-11}	11	3	10^{-3}
10^{-12}	12	2	10^{-2}
10^{-13}	13	1	10^{-1}
10^{-14}	14	0	10^0
10^{-15}	15	-1	10^1

\uparrow
 Acidity
 increases
 ↓
 { Neutral
 solution.
 Pure water }
 ↓
 Acidity
 decreases
 \downarrow

OH^-). In pure water at 25°C, $[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} M$, and the solution is said to be *neutral*. The relationships among $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH , and pOH are given in Table 17.2.*

Example 1. Calculate $[\text{H}_3\text{O}^+]$, $[\text{OH}^-]$, pH , and pOH in 0.0080 M HCl .

HCl is a strong electrolyte, and is completely ionized. Hence

$$[\text{H}_3\text{O}^+] = 0.0080 M$$

$$\begin{aligned}\text{pH} &= -\log [\text{H}_3\text{O}^+] = -\log 0.0080 = -\log (8.0 \times 10^{-3}) \\ &= -\log 8.0 - \log 10^{-3} = -0.90 + 3 = 2.10\end{aligned}$$

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} = \frac{1.01 \times 10^{-14}}{0.0080} = 1.26 \times 10^{-12} M$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log (1.26 \times 10^{-12}) = 11.90$$

Check:

$$\text{pH} + \text{pOH} \stackrel{?}{=} 14$$

$$2.10 + 11.90 = 14.00$$

*In this text,

$$\text{pH} = -\log [\text{H}_3\text{O}^+] \quad (17.5)$$

This is the definition adopted in most textbooks on quantitative analysis. In most textbooks on physical chemistry, however, pH is defined as $-\log a_{\text{H}}$. Thus a_{H} represents the hydrogen-ion activity, and the resultant definition is most accurate for equilibrium calculations. In this book, if it is desired to express a_{H} in terms of its exponent, the quantity is called pa_{H} . This distinction will not often have to be made, however, since activity effects are usually considered negligible. The distinction between pH and pa_{H} is explained more fully by Bates (B5, Chap. 2).

Example 2. What is the $[\text{H}_3\text{O}^+]$ in a solution whose pH is 4.72?

$$\text{pH} = -\log [\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 10^{-\text{pH}} = 10^{-4.72} = 10^{-5+0.28} = 10^{-5} \times 10^{0.28}$$

$$[\text{H}_3\text{O}^+] = 1.91 \times 10^{-5} M$$

17C. IONIZATION OF WEAK MONOPROTIC ACIDS

The ionization of a weak monoprotic acid may be represented by



Numerical values of ionization constants for various acids and bases are given in Appendix VII.

The acidity of a solution of a weak acid depends on its concentration, and on K_a , as shown in the following example.

Example 1. Calculate $[\text{H}_3\text{O}^+]$ in 0.100 M acetic acid, HAc ($K_a = 1.76 \times 10^{-5}$).



Let $[\text{H}_3\text{O}^+] = x M$. Then $[\text{Ac}^-] = x$, since one mole of Ac^- is formed for every mole of H_3O^+ obtained by ionization of the HAc . Likewise, $[\text{HAc}] = 0.100 - x$, since a mole of undissociated HAc must disappear for each mole of H_3O^+ formed. Making these substitutions, Eq. *a* becomes

$$1.76 \times 10^{-5} = \frac{(x)^2}{(0.100 - x)} \quad (b)$$

Eq. *b* is a quadratic that may be simplified. If the acid is weak, it is reasonable to assume that $x \ll 0.100$. Eq. *b* then becomes easy to solve, and

$$x, \text{ or } [\text{H}_3\text{O}^+] = \sqrt{1.76 \times 10^{-5} (0.100 - x)} = 0.00133 M \quad (c)$$

The assumption may be tested after the answer is obtained. In assuming that x , or 0.00133, is negligible compared to 0.100, an error of about 1% is made. Since the uncertainty of the answer is 1:100, the approximation is passable.

If x had not been small compared to 0.100, further approximations would have been necessary, or the quadratic formula might have been used to obtain the answer.

If a salt of the weak acid is added to a solution of the weak acid, its ionization is repressed. The repression is sometimes very effective, even for moderate salt concentrations as shown in the following example.

Example 2. Calculate $[\text{H}_3\text{O}^+]$ in a solution containing 0.100 M HAc and 0.100 M NaAc .



Let $[\text{H}_3\text{O}^+] = y$ *M*. Then $[\text{Ac}^-] = 0.100$ (from the NaAc) $+ y$ (from the ionization of HAc). Similar reasoning gives $[\text{HAc}] = 0.100 - y$. Making these substitutions into Eq. *a*,

$$1.76 \times 10^{-5} = \frac{y(0.100 + y)}{(0.100 - y)} \quad (b)$$

Eq. *b* is a quadratic that may be simplified. Not only is HAc a weak acid, but its ionization is repressed by the presence of the salt, so it is reasonable to assume that $y \ll 0.100$, giving

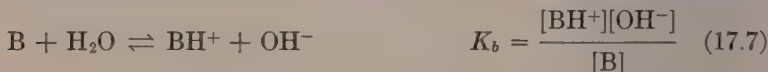
$$y, \text{ or } [\text{H}_3\text{O}^+] = 1.76 \times 10^{-5} \frac{(0.100 - y)}{(0.100 + y)} = 1.76 \times 10^{-5} \text{ } M \quad (c)$$

Comparison of y (i.e., 1.76×10^{-5}) with 0.100 shows the assumption to be justified, so the answer in Eq. *c* is a good one.

Comparison of y with x of Ex. 1 shows that the NaAc depresses the ionization of HAc by about one hundredfold—a great effect.

17D. IONIZATION OF WEAK MONOEQUIVALENT BASES

The ionization of a weak monoequivalent base may be represented by



The basicity of a solution may be calculated from its composition by reasoning similar to that in the preceding examples.

Example 1. Calculate $[\text{OH}^-]$ in a solution containing 0.130 *M* NH_3 and 0.090 *M* NH_4Cl .



Let $[\text{OH}^-] = z$. Then, $[\text{NH}_4^+] = 0.090$ (from the NH_4Cl) $+ z$ (from the ionization of the NH_3). Also, $[\text{NH}_3] = 0.130 - z$. Making these substitutions into Eq. *a*,

$$1.82 \times 10^{-5} = \frac{(0.090 + z)(z)}{(0.130 - z)} \quad (b)$$

It is reasonable to assume that $z \ll 0.090$ and 0.130, in which case Eq. *b* becomes

$$z, \text{ or } [\text{OH}^-] = 1.82 \times 10^{-5} \frac{(0.130 - z)}{(0.090 + z)} = 2.63 \times 10^{-5} \text{ } M \quad (c)$$

A test of the answers shows z (i.e., 2.63×10^{-5}) to be negligible compared to 0.090 and 0.130.

An attempt to find the basic ionization constant for NH_3 in the preceding example revealed that bases are not listed as such in the tables of Appendix VII. Modern tables (B13) give only acid ionization constants for the protonated forms of bases, and basic ionization constants

for the conjugate bases must be calculated through the simple relationship

$$K_a K_b = K_w \quad (\text{For a conjugate pair}) \quad (17.8)$$

However, to save computation, the tables of Appendix VII give not only K_a values for the acids shown, but also K_b values for the conjugate bases.

Example 2. Let an acid be HA, and let its conjugate base be A^- . Show that $K_a K_b = K_w$.



Multiplying Eqs. *a* and *b* together,

$$K_a K_b = \frac{[H_3O^+][A^-]}{[HA]} \cdot \frac{[HA][OH^-]}{[A^-]} = [H_3O^+][OH^-] = K_w$$

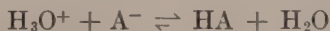
17E. BUFFER SOLUTIONS

17E.1. Description

A buffer solution is one that resists changes in acidity when small amounts of acid or base are added. A solution containing a weak acid (HA) and its salt (NaA) is a buffer solution. Both components are necessary. Any added strong base is neutralized by the HA, and does not increase the $[OH^-]$ of the solution.



Similarly, any added strong acid does not increase the $[H_3O^+]$ of the solution, for H_3O^+ and A^- react to form HA.



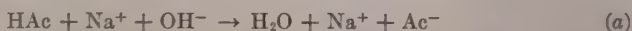
In a buffer solution, the acid in HA is in reserve; it is not free to increase the acidity (i.e., $[H_3O^+]$) of the solution, but it is available to neutralize any strong base that may be added. Likewise, A^- is a reserve base; it does not contribute to $[OH^-]$ in the solution, but it is available to neutralize any strong acid that may be added.

There are also basic buffers containing a weak base (B) and its salt (BHCl).

Actually, of course, a buffer solution does change in pH when acid or base is added, but the change is negligible compared to that in an unbuffered solution. The magnitudes of the changes in pH on the addition of strong base to buffered and unbuffered solutions are compared in the following two examples.

Example 1. Calculate the change in $[\text{H}_3\text{O}^+]$ when the buffer solution in Ex. 2, page 319, is made 0.010 M in NaOH , by the addition of solid NaOH , so that the volume of solution is not changed.

On the addition of the NaOH , the original solution (0.100 M HAc and 0.100 M NaAc) becomes 0.090 M in HAc and 0.110 M in NaAc , since NaOH reacts according to the equation



$$\text{Let } [\text{H}_3\text{O}^+] = z. \text{ Then } [\text{Ac}^-] = 0.110 + z, \text{ and } [\text{HAc}] = 0.090 - z \quad (b)$$

Substituting Eq. b in the ionization-constant expression for HAc , the following equation is obtained.

$$1.76 \times 10^{-5} = \frac{z(0.110 + z)}{(0.090 - z)} \quad (c)$$

$$z, \text{ or } [\text{H}_3\text{O}^+] = 1.44 \times 10^{-5} M \quad (d)$$

The addition of the NaOH therefore lowers $[\text{H}_3\text{O}^+]$ from $1.76 \times 10^{-5} M$ (see Ex. 2, p. 319) to $1.44 \times 10^{-5} M$, or

$$\frac{1.76 \times 10^{-5} - 1.44 \times 10^{-5}}{1.76 \times 10^{-5}} \times 100 = 18\%$$

Example 2. Calculate the change in $[\text{H}_3\text{O}^+]$ when an unbuffered solution having the same $[\text{H}_3\text{O}^+]$ as the original solution in Ex. 1 is made 0.010 M in NaOH .

An unbuffered solution having $[\text{H}_3\text{O}^+] = 1.76 \times 10^{-5} M$ would contain $1.76 \times 10^{-5} M$ HCl , or some other strong acid. When the NaOH is added, neutralization occurs, and excess NaOH is left.



In the resulting solution, $\text{NaCl} = 1.76 \times 10^{-5} M$, and $\text{NaOH} = 0.010 - 1.76 \times 10^{-5} = 0.010 M$. Hence, after addition of NaOH , $[\text{OH}^-] = 0.010 M$.

$$[\text{H}_3\text{O}^+] = \frac{1.01 \times 10^{-14}}{0.010} = 1.0 \times 10^{-12} M$$

The decrease in $[\text{H}_3\text{O}^+]$ is from $1.75 \times 10^{-5} M$ (acid) to $1.0 \times 10^{-12} M$ (basic), about a 10^7 -fold decrease. In comparison, the 18% change in the buffered solution is extremely small.

17E.2. Preparation

The choice of a buffering medium for a particular application involves considerations other than just the desired $p\text{H}$. In order of importance, these considerations are:

1. The buffering components must not interfere chemically with the system to be buffered. Thus if it is desired to buffer a system containing Ca^{2+} at a $p\text{H}$ of 10, it would not be permissible to use a phosphate buffer, for $\text{Ca}_3(\text{PO}_4)_2$ would precipitate.

2. It is best to choose buffering components for which pK_a of the

weak acid is as close as possible to the desired pH , or for which pK_b of the weak base is as close as possible to the desired pOH . Under this condition, $[HA]/[A^-]$ is close to unity, and the buffering capacity is a maximum. Proof of this statement is given in the Supplement (p. 768).

3. For high buffering capacity, the concentrations of the buffering substances should be high. The buffering capacity is high if addition of a large amount of strong acid or base produces only a small percentage change in $[H_3O^+]$. The dependence of $[H_3O^+]$ and capacity upon concentration is brought out in the following two examples.

Example 1. What concentrations of HAc and NaAc should be used to prepare a buffer with $[H_3O^+] = 1.76 \times 10^{-5} M$?

The only requirement is that the ionization-constant expression for HAc be satisfied.

$$1.76 \times 10^{-5} = \frac{[H_3O^+][Ac^-]}{[HAc]} = \frac{(1.76 \times 10^{-5})[Ac^-]}{[HAc]}$$

$$\frac{[HAc]}{[Ac^-]} = 1.00$$

Any of an infinite number of solutions of HAc and NaAc may be chosen to fulfill this requirement. A 0.100 M HAc–0.100 M NaAc solution is one. Any solution in which the concentration of HAc is equal to that for NaAc is also satisfactory.*

Example 2. To give the $[H_3O^+]$ desired in Ex. 1, it is decided to use 1.00 M HAc and 1.00 M NaAc. Show that the change in $[H_3O^+]$ on making this buffer 0.010 M in NaOH is less than the 18% change produced in the 0.100 M HAc–0.100 M NaAc buffer of Ex. 1, page 322.

After addition of the NaOH, the composition of the solution becomes

$$HAc = 0.99 M, \text{ and } NaAc = 1.01 M$$

By letting $w = [H_3O^+]$ in the solution after the NaOH is added, the ionization-constant expression becomes

$$1.76 \times 10^{-5} = \frac{w(1.01 + w)}{(0.99 - w)}$$

$$w, \text{ or } [H_3O^+] = 1.72 \times 10^{-5} M$$

Hence the addition of the NaOH changes $[H_3O^+]$ from $1.76 \times 10^{-5} M$ (Ex. 1) to $1.72 \times 10^{-5} M$, a decrease of only about 2%. This is considerably less than the 18% change produced by the same amount of base in 0.100 M HAc–0.100 M NaAc, and the capacity of the 1.00 M HAc–1.00 M NaAc solution is therefore much higher.

*In this problem it is assumed that only a negligible proportion of the HAc ionizes. For low concentrations of HAc and/or NaAc, this assumption may break down. Buffers, however, are always fairly concentrated solutions.

4. After preparation, the buffer system selected should be checked with a pH meter or indicators to ascertain that it has the proper pH . Adjustments in composition should be made to bring the pH within the proper range, if necessary. There is not enough specific information on activity coefficients to permit accurate computation of the pH , especially if the buffer components are concentrated. The results of computations such as the preceding ones may be several-fold in error. These computations are given for illustrative purposes only, and are not necessarily accurate.

The chemical literature abounds with tables giving compositions of buffer systems against pH . To obtain a buffer of any desired pH , a solution of the specified composition is prepared. Bates (B5, Chap. 5) gives much information on the preparation and properties of buffer solutions. Table 17.3 gives compositions of some buffer systems and the pH ranges in which they are used.

Buffer tablets are available at nominal prices from chemical supply houses. To prepare a buffer solution, a tablet is simply dissolved in water and made up to a specified volume.

TABLE 17.3*
SOME BUFFER SYSTEMS

Acid component	Basic component	pH range
HCl	Glycine	1.0–3.7
HCl	KH phthalate	2.2–4.0
Citric acid	NaOH	2.2–6.5
HAc	NaAc	4.0–6.2
KH phthalate	NaOH	4.0–6.2
NaH ₂ PO ₄	Na ₂ HPO ₄	5.9–8.0
HBO ₂	NaOH	8.0–10.0
Glycine	NaOH	8.2–10.1
Na ₂ HPO ₄	NaOH	11.0–12.0

*Data taken from R. G. Bates, *Electrometric pH Determinations* (New York: Wiley, 1954), Table 11, with permission of the publisher.

For very accurate work, the National Bureau of Standards recommends certain solutions to give buffers at particular pH values that are rather insensitive to changes in composition and temperature (B5). Thus, the pH of 0.05 M KH phthalate is 4.00–4.01 over a temperature range from 10° to 30°C. At 25°, the pH values of 0.01, 0.05, and 0.1 M KH phthalate are 4.117, 4.005, and 3.948, respectively (U5). KHP solutions are easy to prepare, but are susceptible to attack by molds, which may seriously affect the pH even before there is visible evidence of mold growth. Thymol (0.6 g/l) may be used as a preservative (M4).

17E.3. Importance

Buffer solutions are used widely in quantitative analysis. In the iodine-arsenite titration the acid produced hinders the reaction. Such reactions must be brought about in buffered media to ensure removal of the acid as fast as it is formed. Also, many precipitates must be formed in buffered solutions to prevent contamination; the precipitation of MgNH_4PO_4 is an example. Many separations depend critically upon $p\text{H}$, which must be controlled so that some components are soluble while others remain insoluble; separations based upon precipitation with H_2S are examples.

The importance of buffer solutions extends far beyond quantitative analysis. Most biological and physiological processes are critically dependent upon $p\text{H}$. A difference of a few tenths of a $p\text{H}$ unit from the normal may result in the death of an organism. The yield of an industrial fermentation process, or of a process for antibiotic production, may drop greatly if the $p\text{H}$ departs appreciably from the optimum. Rate of food spoilage, rate of reproduction of bacteria, digestion, etc., are all highly dependent upon $p\text{H}$. All these processes occur in buffered media.

Most body fluids are buffers. An excellent example is the blood, which contains phosphates, carbonates, and proteins as buffering components. The blood has a remarkably constant $p\text{H}$ of 7.3–7.5, even though there are large amounts of acids and bases that are constantly introduced by absorption and digestion of foods, muscular activity, and respiration. One of the functions of the blood is to remove waste CO_2 from the cells, and to carry the CO_2 to the lungs, where it is lost by respiration to the air. If its $p\text{H}$ drops below 7.3, the blood is too acid effectively to remove CO_2 (an acid anhydride) from the cells. If the $p\text{H}$ rises above 7.5, the blood is too basic to give up CO_2 effectively in the lungs. In either case, the organism responds in an attempt to return the $p\text{H}$ to the normal range, and the accompanying disturbances are the symptoms of illness. A $p\text{H}$ outside the range of 7.0–7.8 is fatal unless promptly relieved.

17F. ACID-BASE PROPERTIES OF SALTS. HYDROLYSIS

If the salt (NaA) of a weak acid (HA) and a strong base (NaOH) is put into water, the solution does not remain neutral; A^- has basic properties, and the solution becomes basic.

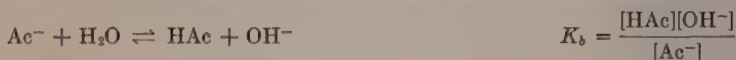


If HA is an electrolyte that is comparable in weakness to water, then reaction 17.9 goes appreciably to the right, $[\text{OH}^-]$ becomes comparable to $[\text{A}^-]$ in magnitude, and the solution becomes strongly basic. For most stable salts, however, HA is only moderately weak, and A^- cannot compete effectively with OH^- for the proton; then reaction 17.9 lies only slightly to the right, and $[\text{OH}^-]$ is small compared to $[\text{A}^-]$.^{*} It is important to point out that even though reaction 17.9 may occur slightly, enough OH^- may be formed to alter the pH of the water greatly when the salt is dissolved, as shown in the following examples. Salt solutions are not always neutral; owing to hydrolysis, they may be considerably more basic or acidic than pure water.

If the salt (BHCl) of a weak base (B) and a strong acid (HCl) is put into water, hydrolysis gives an acid reaction.



Example 1. Calculate $[\text{H}_3\text{O}^+]$ and the degree of hydrolysis of 0.100 M NaAc.



Let $[\text{OH}^-] = x$. Then $[\text{HAc}] = x$, since one mole of HAc is produced for each mole of OH^- formed. Similarly, $[\text{Ac}^-] = 0.100 - x$. K_b may be found in Appendix VIIB, and the above equation becomes

$$5.7 \times 10^{-10} = \frac{x^2}{(0.100 - x)}$$

$$x, \text{ or } [\text{OH}^-] = 7.5 \times 10^{-6} M$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.01 \times 10^{-14}}{7.5 \times 10^{-6}} = 1.35 \times 10^{-9} M$$

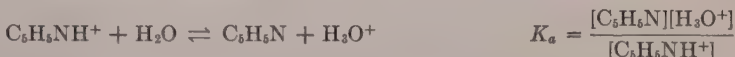
^{*}Classically, the reaction of a salt with water, as in Eq. 17.9, is called *hydrolysis*. Hydrolysis represents a process entirely different from the classical splitting type of ionization reaction. Hydrolysis may be treated quantitatively in classical theory by setting up an hydrolysis constant (B15). Brönsted theory is simpler, however, since hydrolysis is simply an acid or base ionization process.

Semantically, if one thinks in Brönsted terms, it might be desirable to do away with the term "hydrolysis," but this is impossible because it appears so widely in the literature. In this text, "hydrolysis" is used to represent the acid or base ionization of a salt in water. Thus, if we say that HA ionizes in water according to Eq. 17.1, then the term hydrolysis may designate the ionization of the conjugate base A^- according to Eq. 17.9. Likewise, if we say that the base B ionizes according to Eq. 17.2, then the term hydrolysis may designate the ionization of the conjugate acid BH^+ , according to Eq. 17.10. The hydrolysis of metal ions according to Brönsted is described in the Supplement (p. 769).

$$\begin{aligned}\% \text{ hydrolysis} &= \frac{\text{conc. of NaAc hydrolyzed (i.e., } [\text{OH}^-])}{\text{total NaAc conc.}} \times 100 \\ &= \frac{7.5 \times 10^{-6}}{0.100} \times 100 = 0.0075\%\end{aligned}$$

In spite of the small degree of hydrolysis, $[\text{OH}^-]$ is 75-fold greater in this salt solution than in pure water.

Example 2. Pyridine forms a salt with HCl—pyridinium hydrochloride, $\text{C}_5\text{H}_5\text{NHCl}$. The salt is a strong electrolyte that ionizes completely in water. What is the pH of 0.100 *M* pyridinium hydrochloride?



If $[\text{H}_3\text{O}^+] = x$, then $[\text{C}_5\text{H}_5\text{N}] = x$, and $[\text{C}_5\text{H}_5\text{NH}^+] = 0.100 - x$. K_a may be found in Appendix VIIB, giving

$$6.2 \times 10^{-6} = \frac{x^2}{(0.100 - x)}$$

$$x, \text{ or } [\text{H}_3\text{O}^+] = 7.9 \times 10^{-4} \text{ } M$$

$$\text{pH} = -\log [\text{H}_3\text{O}^+] = -\log (7.9 \times 10^{-4}) = -(0.90 - 4.000) = 3.10$$

Note that this solution is rather acid. The salts of pyridine are stronger as acids than pyridine is as a base.

17G. MULTIPLE EQUILIBRIA

17G.1. Failure of the Elementary Methods

In the preceding elementary methods of handling acid-base equilibria, it is tacitly assumed that only one equilibrium is important. This assumption gains simplicity, for simultaneous equations never arise. However, the elementary methods sometimes fail, as shown in the two following examples.

Example 1. Calculate $[\text{H}_3\text{O}^+]$ in $1.00 \times 10^{-5} \text{ } M$ HBO_2 .



Let $[\text{H}_3\text{O}^+] = x$. Then $[\text{BO}_2^-] = x$, and $[\text{HBO}_2] = 1.00 \times 10^{-5} - x$. Substituting these concentrations into the ionization-constant expression and solving, we obtain

$$6.5 \times 10^{-10} = \frac{(x)(x)}{1.00 \times 10^{-5} - x}$$

$$x, \text{ or } [\text{H}_3\text{O}^+] = 8.1 \times 10^{-8} \text{ } M$$

This is an impossible answer, for no acid, no matter how weak, can give a basic solution just by ionizing in water. A test of the answer reveals the source of error. If $[\text{H}_3\text{O}^+]$ is really $8.1 \times 10^{-8} M$, then $[\text{OH}^-]$ is $1.0 \times 10^{-14}/8.1 \times 10^{-8}$, or $1.2 \times 10^{-7} M$. In furnishing this $[\text{OH}^-]$ by ionization, water must furnish the same $[\text{H}_3\text{O}^+]$, or $1.2 \times 10^{-7} M$. Water therefore contributes more to the total $[\text{H}_3\text{O}^+]$ than does the HBO_2 itself. The elementary method gives a poor answer because it does not consider that $[\text{H}_3\text{O}^+]$ is contributed to significantly by two sources—the ionization of HBO_2 and the ionization of water.

Example 2. Calculate $[\text{H}_3\text{O}^+]$ in $0.100 M \text{NaHCO}_3$.

It could be assumed that the principal reaction is



Let $x = [\text{H}_3\text{O}^+]$. Then $[\text{CO}_3^{2-}] = x$, and $[\text{HCO}_3^-] = 0.100 - x$. Substituting these concentrations into the ionization-constant expression and solving,

$$6.0 \times 10^{-11} = \frac{(x)(x)}{(0.100 - x)}$$

$$x, \text{ or } [\text{H}_3\text{O}^+] = 2.4 \times 10^{-6} M$$

However, it happens that NaHCO_3 solutions are definitely basic ($p\text{H}$ 8–9), and that the value calculated above for $[\text{H}_3\text{O}^+]$ is more than one thousandfold in error.

A test of the answers reveals the source of error. If $[\text{H}_3\text{O}^+]$ and $[\text{HCO}_3^-]$ are as calculated, then $[\text{H}_2\text{CO}_3]$ must be fixed by the equilibrium



$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{3.5 \times 10^{-7}} = \frac{(2.4 \times 10^{-6})(0.100)}{3.5 \times 10^{-7}} = 0.7 M$$

This $[\text{H}_2\text{CO}_3]$ is several times greater than the given total concentration of NaHCO_3 , which is impossible, indicating that the equilibrium on which all the calculations were based is not the important one at all.

The correct solution of this problem is given on page 333.

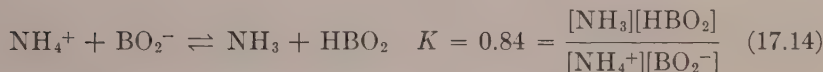
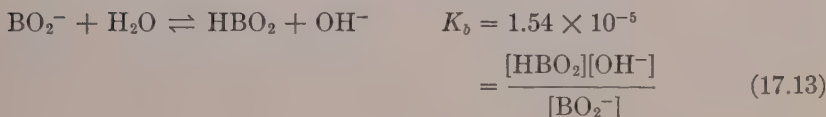
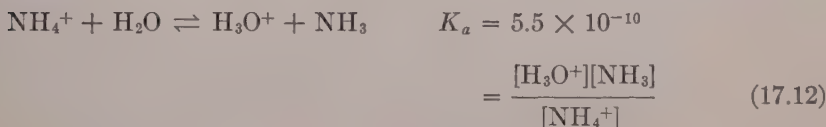
17G.2. The Method of the Principal Equilibrium (F10)

The method of the principal equilibrium is simply the elementary method, with two modifications: (1) a systematic procedure for choosing the principal equilibrium, and (2) a systematic check of the answer to verify that the chosen equilibrium is really the predominant one. The method is outlined in the following paragraphs, illustrated by a calculation of $[\text{H}_3\text{O}^+]$ in a $0.100 M \text{NH}_4\text{BO}_2$ solution. Another example is given on page 330.

1. Designate the *major solute species*, which are the ones present in major proportions. For $0.100 M \text{NH}_4\text{BO}_2$, these are $0.100 M \text{NH}_4^+$ and $0.100 M \text{BO}_2^-$.

2. Choose the *principal equilibrium*. Write the following types of reactions for each of the major species: (a) ionization of an acid, base, or water, with equilibrium constants K_a , K_b , or K_w . If an acid (or base) dissociates in steps, the successive ionization constants are K_1 , K_2 , (b) Reaction of one acid or base with another. The equilibrium constants for such reactions are calculable from the K_a and K_b values of the acids and bases involved (see below).

For the 0.100 M NH_4BO_2 solution, the possible reactions are



$$\begin{aligned} \left(K = \frac{[\text{NH}_3][\text{HBO}_2]}{[\text{NH}_4^+][\text{BO}_2^-]} \cdot \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} \cdot \frac{[\text{OH}^-]}{[\text{OH}^-]} = \frac{K_a K_b}{K_w} \right. \\ \left. = \frac{5.5 \times 10^{-10} \times 1.54 \times 10^{-5}}{1.01 \times 10^{-14}} = 0.84 \right) \end{aligned}$$

The principal equilibrium is usually the one with the largest equilibrium constant, or Eq. 17.14. The choice of the principal equilibrium is the critical step. If there is no principal equilibrium, or if an incorrect choice is made, it is revealed later, and a different approach may be tried.

3. Calculate the concentrations of the *principal species* that appear in the principal equilibrium, assuming that the principal equilibrium is the only one. Thus, in Eq. 17.14, if we let $[\text{NH}_3] = x$, then $[\text{HBO}_2] = x$, $[\text{NH}_4^+] = 0.100 - x$, and $[\text{BO}_2^-] = 0.100 - x$. Making these substitutions into the equilibrium-constant expression,

$$0.84 = \frac{x^2}{(0.100 - x)^2}$$

$$x, \text{ or } [\text{NH}_3], \text{ or } [\text{HBO}_2] = 0.048 \text{ M}$$

$$0.100 - x, \text{ or } [\text{NH}_4^+], \text{ or } [\text{BO}_2^-] = 0.052 M$$

4. Calculate the concentrations of all other *minor solute species* from the principal species concentrations and the appropriate equilibrium constants. Thus, $[\text{H}_3\text{O}^+]$ may be calculated from Eq. 17.12, and the known values for $[\text{NH}_4^+]$ and $[\text{NH}_3]$.

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 5.5 \times 10^{-10} \frac{(0.052)}{(0.048)} = 6.0 \times 10^{-10} M$$

From Eq. 17.11, $[\text{OH}^-] = 1.01 \times 10^{-14}/[\text{H}_3\text{O}^+] = 1.69 \times 10^{-5} M$.

5. If all minor species concentrations are negligible compared to the concentrations of those principal species that are derived from the major species, then the answers are acceptable. Both $[\text{OH}^-]$ and $[\text{H}_3\text{O}^+]$ are unimportant compared to $[\text{NH}_4^+]$, $[\text{BO}_2^-]$, $[\text{HBO}_2]$, and $[\text{NH}_3]$, indicating that the answers are good ones.

6. If any of the minor species concentrations is not negligible, one of three paths must be followed to obtain a suitable answer.

(a) If any minor species concentration is not negligible, but is still small, successive approximations may be used to obtain the correct answer, as in the following example.

(b) If any minor species has a larger concentration than a principal species, the choice of the principal equilibrium should be reexamined, and another choice made.

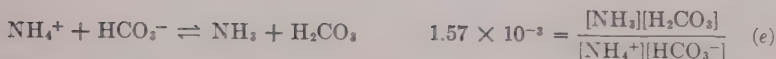
(c) If no single principal equilibrium may be found, the methods described in the Supplement (p. 769) may be tried.

The method of the principal equilibrium does not always yield a correct answer, but incorrect answers will always be revealed. An answer may be found and tested quickly, and the method of the principal equilibrium is therefore recommended as a first step in solving multiple-equilibrium problems.

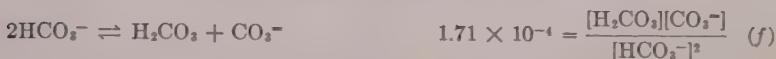
Example. Calculate $[\text{H}_3\text{O}^+]$ in 0.0100 M NH_4HCO_3 .

There are six possible equilibria.





$$\left(\frac{[\text{NH}_3][\text{H}_2\text{CO}_3]}{[\text{NH}_4^+][\text{HCO}_3^-]} \cdot \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{K_{\text{NH}_4^+}}{K_{\text{H}_2\text{CO}_3}} = \frac{5.5 \times 10^{-10}}{3.5 \times 10^{-7}} = 1.57 \times 10^{-3} \right)$$



$$\left(\frac{[\text{H}_2\text{CO}_3][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]^2} \cdot \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{K_{\text{HCO}_3^-}}{K_{\text{H}_2\text{CO}_3}} = \frac{6.0 \times 10^{-11}}{3.5 \times 10^{-7}} = 1.71 \times 10^{-4} \right)$$

Eq. *e* may be chosen as the principal equilibrium. Let $x = [\text{NH}_3]$. Then $[\text{H}_2\text{CO}_3] = x$, and $[\text{NH}_4^+] = [\text{HCO}_3^-] = 0.0100 - x$, and Eq. *e* becomes

$$1.57 \times 10^{-3} = \frac{x^2}{(0.0100 - x)^2}$$

$$x, \text{ or } [\text{NH}_3], \text{ or } [\text{H}_2\text{CO}_3] = 3.8 \times 10^{-4} M$$

$$0.0100 - x, \text{ or } [\text{NH}_4^+], \text{ or } [\text{HCO}_3^-] = 0.0096 M$$

To find if any other minor species are significant, find $[\text{CO}_3^{2-}]$ from Eq. *f*, which is the second most important equilibrium.

$$[\text{CO}_3^{2-}] = 1.71 \times 10^{-4} \frac{[\text{HCO}_3^-]^2}{[\text{H}_2\text{CO}_3]} = 1.71 \times 10^{-4} \frac{(0.0096)^2}{3.8 \times 10^{-4}} = 4.1 \times 10^{-6} M$$

$[\text{CO}_3^{2-}]$ is not negligible compared to the principal species NH_3 or H_2CO_3 , and a second approximation is necessary. If $[\text{NH}_3] = y$, then inspection of Eqs. *e* and *f* shows that $[\text{H}_2\text{CO}_3]$ should be approximated as $y + 4.1 \times 10^{-6}$. Similarly, $[\text{NH}_4^+] = 0.0100 - y$, and $[\text{HCO}_3^-] = 0.0100 - y - 2(4.1 \times 10^{-6})$, and Eq. *e* becomes

$$1.57 \times 10^{-3} = \frac{(y)(y + 4.1 \times 10^{-6})}{(0.0100 - y)(0.0100 - y - 8.2 \times 10^{-6})}$$

$$y, \text{ or } [\text{NH}_3] = 3.6 \times 10^{-4} M$$

$$[\text{H}_2\text{CO}_3] = y + 4.1 \times 10^{-6} = 4.0 \times 10^{-4} M$$

$$[\text{NH}_4^+] = 0.0100 - y = 0.0096 M$$

$$[\text{HCO}_3^-] = 0.0100 - y - 8.2 \times 10^{-6} = 0.0096 M$$

$$[\text{CO}_3^{2-}] = 1.71 \times 10^{-4} \frac{[\text{HCO}_3^-]^2}{[\text{H}_2\text{CO}_3]} = \frac{1.71 \times 10^{-4} (0.0096)^2}{4.0 \times 10^{-4}} = 3.9 \times 10^{-6} M$$

The second estimates are consistent because $[\text{CO}_3^{2-}]$ does not differ greatly from the first estimate.

The concentrations of any other minor species can now be calculated. Thus, from Eq. *b*,

$$[\text{H}_3\text{O}^+] = 5.5 \times 10^{-10} \frac{[\text{NH}_4^+]}{[\text{NH}_3]} = 5.5 \times 10^{-10} \frac{(0.0096)}{(3.6 \times 10^{-4})} = 1.47 \times 10^{-8} M$$

17G.3. Ionic Strength Effects

All previously described methods of handling acid-base equilibria have neglected the effect of ionic strength. Corrections based upon activity coefficients are described in the Supplement (p. 775).

17H. POLYPROTIC ACIDS

A polyprotic acid has more than one ionizable proton per molecule. Such acids ionize in steps, each step characterized by its own ionization constant. For example, H_2CO_3 ionizes as follows:



The removal of protons becomes increasingly difficult with successive steps, since the charge on the residual ion increases. Hence the ionization constant of any step for a particular acid is less than that for the preceding step. For most inorganic polyprotic acids, successive K 's differ greatly, the ratios being of the order of 10^4 (see H_2CO_3 , H_3PO_4 , Appendix VIIA, p. 923). Pauling gives an excellent classification of many inorganic acids according to strength (P3). On the other hand, many organic polyprotic acids have successive K 's that are not highly different, especially if the protonated groups are widely separated in the molecule. (See tartaric and citric acids, Appendix VIIB.) Polyprotic bases have similar properties.

Equilibria involving polyprotic acids may be treated by the method of the principal equilibrium. Often, if there are great differences between successive K_a 's, the principal equilibrium may be chosen by inspection, as in the following examples.

Example 1. What is $[\text{H}_3\text{O}^+]$ in 0.100 M H_3PO_4 ?

Assume that only one equilibrium is important, since K_1 is so much greater than K_2 and K_3 .



Let $x = [\text{H}_3\text{O}^+]$. Then $[\text{H}_2\text{PO}_4^-] = x$, and $[\text{H}_3\text{PO}_4] = 0.100 - x$. Substituting these concentrations into the ionization-constant expression and solving, we obtain

$$\frac{(x)(x)}{0.100 - x} = 0.0071$$

$$x, \text{ or } [\text{H}_3\text{O}^+] = 0.0233 M$$

With the calculated value for $[\text{H}_3\text{O}^+]$, the assumption that only one equilibrium is important may be tested by finding if there are appreciable amounts of phosphate in forms other than H_3PO_4 and H_2PO_4^- . Thus

$$[\text{HPO}_4^-] = K_2 \frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{O}^+]} = 6.2 \times 10^{-8} \frac{0.0233}{0.0233} = 6.2 \times 10^{-8} M$$

This concentration of HPO_4^- is certainly negligible compared to the concentrations of H_3PO_4 (0.077 M) and H_2PO_4^- (0.0233 M). Similarly, it may be shown that $[\text{PO}_4^{3-}]$ is extremely low. This indicates that H_3PO_4 and H_2PO_4^- are the only significant phosphate-bearing species, justifying the assumption. Were this not the case, the elementary method would not be applicable, and it could not be assumed that $[\text{H}_3\text{O}^+] = [\text{H}_2\text{PO}_4^-] = x$.

Example 2. What is $[\text{H}_3\text{O}^+]$ in a solution containing 0.035 M NaH_2PO_4 and 0.196 M Na_2HPO_4 ?

Both conjugates of the second ionization step are present at finite concentrations, so we have a buffer solution whose acidity is set by the ratio of these concentrations.



Let $[\text{H}_3\text{O}^+] = x$. Then $[\text{HPO}_4^-] = 0.196 + x$, and $[\text{H}_2\text{PO}_4^-] = 0.035 - x$.

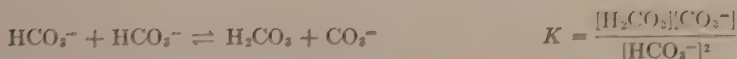
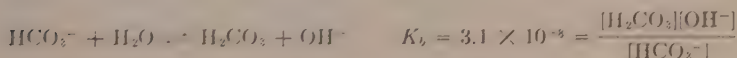
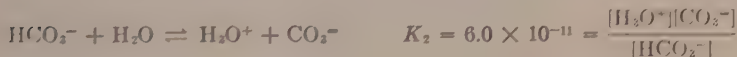
$$6.2 \times 10^{-8} = \frac{x(0.196 + x)}{(0.035 - x)}$$

$$x, \text{ or } [\text{H}_3\text{O}^+] = 1.11 \times 10^{-8} M$$

With values of K_1 and K_3 from Appendix VIIA, it may be shown that the concentrations of other phosphate-bearing species (i.e., H_3PO_4 and PO_4^{3-}) are negligible compared to the principal species.

Example 3. What is $[\text{H}_3\text{O}^+]$ in a solution containing 0.100 M NaHCO_3 ?

The possibilities for the principal equilibrium are:



$$\left(K = \frac{[\text{H}_2\text{CO}_3]}{[\text{HCO}_3^-]} \cdot \frac{[\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} \cdot \frac{[\text{H}_3\text{O}^+]}{[\text{H}_3\text{O}^+]} = \frac{K_2}{K_1} = \frac{6.0 \times 10^{-11}}{3.5 \times 10^{-7}} = 1.71 \times 10^{-4} \right)$$

Assuming that the last equilibrium is the principal one, let $x = [\text{H}_2\text{CO}_3] = [\text{CO}_3^{2-}]$. Then $[\text{HCO}_3^-] = 0.100 - 2x$, and

$$1.71 \times 10^{-4} = \frac{x^2}{(0.100 - 2x)^2}$$

$$x, \text{ or } [\text{H}_2\text{CO}_3], \text{ or } [\text{CO}_3^{2-}] = 0.00128 \text{ } M$$

$$0.100 - 2x, \text{ or } [\text{HCO}_3^-] = 0.097 \text{ } M$$

With the now known concentrations for the principal species, $[\text{H}_3\text{O}^+]$ may be calculated from the equilibrium constant for the second ionization step of H_2CO_3 .

$$[\text{H}_3\text{O}^+] = K_2 \frac{[\text{HCO}_3^-]}{[\text{CO}_3^{2-}]} = 6.0 \times 10^{-11} \frac{0.097}{0.00128} = 4.5 \times 10^{-9} \text{ } M$$

If a polyprotic acid is partially neutralized, or put into a buffered solution, the $p\text{H}$ determines the form that the polyprotic acid assumes. In systems containing carbonate, for example, Eqs. 17.15 and 17.16 (p. 332) are the important equilibria that determine the concentrations of the carbonate-bearing species. In strongly acid solutions (where $[\text{H}_3\text{O}^+] \gg K_1, K_2$), H_2CO_3 is the predominant form. In strongly basic

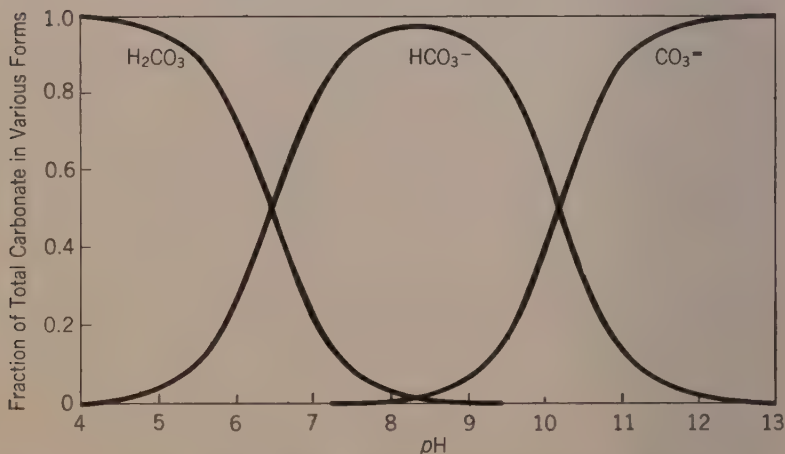
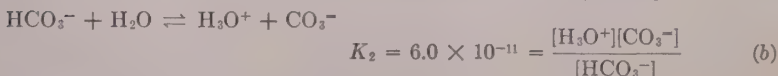
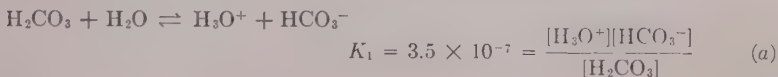


FIG. 17.1. Solute Species Present in Carbonate Systems as a Function of $p\text{H}$ —Calculated, for $K_1 = 3.5 \times 10^{-7}$ and $K_2 = 6.0 \times 10^{-11}$.

solutions (where $[\text{H}_3\text{O}^+] \ll K_1, K_2$), CO_3^{2-} predominates. In the region where $K_1 < [\text{H}_3\text{O}^+] < K_2$, HCO_3^- is the predominant species. Figure 17.1 shows how the proportion of the carbonate in each form depends upon $p\text{H}$. The following example illustrates how points may be calculated to delineate the curves of Fig. 17.1.

Example 4. Calculate the concentrations of the various carbonate-bearing species when a system perfectly buffered at pH 7.00 is made 0.0100 M in Na_2CO_3 .



A material balance on carbonate gives

$$[H_2CO_3] + [HCO_3^-] + [CO_3^{2-}] = 0.0100 \quad (c)$$

If the pH is set to 7.00, Eqs. a and b give

$$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{K_1}{[H_3O^+]} = \frac{3.5 \times 10^{-7}}{10^{-7}} = 3.5 \quad (d)$$

$$\frac{[CO_3^{2-}]}{[HCO_3^-]} = \frac{K_2}{[H_3O^+]} = \frac{6.0 \times 10^{-11}}{10^{-7}} = 6.0 \times 10^{-4} \quad (e)$$

The concentrations of the various carbonate species may now be calculated from Eqs. c , d , and e .

$$[H_2CO_3] = 0.0022 M$$

$$[HCO_3^-] = 0.0078 M$$

$$[CO_3^{2-}] = 4.7 \times 10^{-6} M$$

Thus, 22% of the total carbonate exists as H_2CO_3 , 78% as HCO_3^- , and only 0.047% as CO_3^{2-} . Distributions of carbonate among the various forms may be calculated likewise for other pH values and plotted as in Fig. 17.1.

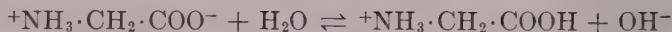
171. AMPHIPROTIC SUBSTANCES

Many substances are amphoteric, like water, and can act either as acids or bases. Inorganic examples, taken from Appendix VIIA, are: HCO_3^- , hydrazinium ion ($N_2H_4 \cdot H^+$), $H_2PO_4^-$, and HPO_4^{2-} .

Organic substances that have both acid and basic groups within a single molecule are amphoteric. An example is glycine ($NH_2 \cdot CH_2 \cdot COOH$), a biologically important amino acid. In aqueous solution, the proton tends to associate with the basic amino group rather than with the carboxylate group, and the molecule exists principally in the zwitter-ion form, $^+NH_3 \cdot CH_2 \cdot COO^-$. Glycine may act as either an acid or a base, the ionization constants being given in Appendix VIIB:



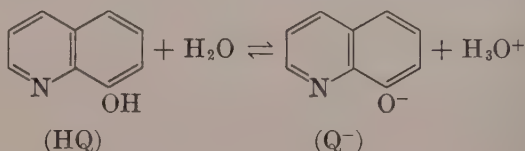
$$K_a = 1.66 \times 10^{-10} = \frac{[NH_2 \cdot CH_2 \cdot COO^-][H_3O^+]}{[^+NH_3 \cdot CH_2 \cdot COO^-]}$$



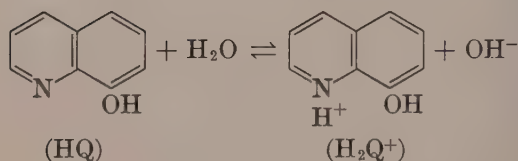
$$K_b = 2.2 \times 10^{-12} = \frac{[^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COOH}][\text{OH}^-]}{[^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COO}^-]}$$

The titration of amino acids is described in the Supplement (p. 788).

Another example is 8-hydroxyquinoline, which is widely used as a metal-ion complexer, and whose ionization constants are given in Appendix VIIB:



$$K_a = 6 \times 10^{-11} = \frac{[\text{H}_3\text{O}^+][\text{Q}^-]}{[\text{HQ}]}$$



$$K_b = 9.3 \times 10^{-10} = \frac{[\text{H}_2\text{Q}^+][\text{OH}^-]}{[\text{HQ}]}$$

As shown in the following example, the form assumed by an amphoteric substance depends on the pH.

Example. Calculate mentally the proportion of glycine in its various forms at pH 2.35 and 5.

The distributions are based upon the two acid dissociation constants (Appendix VIIB):



$$K_1 = 10^{-2.35} = \frac{[\text{H}_3\text{O}^+][^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COO}^-]}{[^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COOH}]} \quad (a)$$



$$K_2 = 10^{-9.78} = \frac{[\text{H}_3\text{O}^+][\text{NH}_2\cdot\text{CH}_2\cdot\text{COO}^-]}{[^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COO}^-]} \quad (b)$$

At pH 2.35, it may be seen from Eq. *a* that $[\text{H}_3\text{O}^+]/[\text{H}_2\text{O}]$ is unity, so half of the glycine is in the acid form and half in the neutral

(zwitter-ion) form. From Eq. *b*, the concentration of the basic form is only $10^{-7.4}$ as great as the neutral form.

At pH 5, it may be seen from Eq. *a* that the ratio of the neutral to the acid form is $10^{2.65}$, so only a few tenths of a per cent is in the acid form. Likewise, from Eq. *b*, the ratio of the basic to the neutral form is $10^{-4.78}$, so only a few thousandths of a per cent is in the basic form. More than 99% is in the neutral form ($^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COO}^-$).

QUESTIONS

Section 17A

1. What is the essential difference in degree of ionization between $\text{Mg}(\text{OH})_2$, whose behavior in solution is described by a solubility product, and acetic acid, whose behavior is described by an ionization constant?
2. Give the conjugate bases of the following acids: H_2PO_4^- , H_2O , NH_4^+ , glycolic acid ($\text{HO}\cdot\text{CH}_2\cdot\text{COOH}$), ethanolaminium ion ($\text{HO}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{NH}_3^+$), glycine ($^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COO}^-$).
3. Give the conjugate acids of the following bases: H_2PO_4^- , H_2O , ethylamine ($\text{C}_2\text{H}_5\cdot\text{NH}_2$), oxalate ($^-\text{OOC}\cdot\text{COO}^-$), glycine ($^+\text{NH}_3\cdot\text{CH}_2\cdot\text{COO}^-$).
4. Write equations to show the acid-base behavior of each of the following substances in water: CO_2 , NH_4Cl , Na_2CO_3 , succinic acid ($\text{HOOC}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{COOH}$), aniline ($\text{C}_6\text{H}_5\cdot\text{NH}_2$), SO_3^- .

Section 17B

1. What are the advantages of expressing acidity in terms of *pH*, rather than $[\text{H}_3\text{O}^+]$?
2. What is the meaning of a negative *pH*?
3. Assuming 100% ionization of the solutes used, describe the preparation of a solution of *pH* (a) 15.00, using solid NaOH ; (b) -1.0 , using conc. HCl .
4. What is incorrect about the statement, "The *pH* of pure water is 7.0"? Give conditions under which this statement is not true.
5. Give examples of four amphiprotic substances, illustrating the behavior of each with equations.
6. Very pure liquid NH_3 is a conductor, indicating that it is ionized and therefore amphiprotic. Speculate on the nature of the ionization, and check with the literature (L15).

Sections 17C, D

1. Explain the difference, if any, between a solution of a weak monoprotic acid with a *pH* of 2.00, and a solution of that acid at a concentration of 0.0100 *M*. Repeat the explanation for a strong acid such as HCl .
2. Why does an HAc solution have a higher *pH* than an HCl solution of the same molarity? How does the *pH* of a 0.0100 *N* H_2SO_4 solution compare with that of 0.0100 *N* HCl ?
3. How does the addition of BCl affect the *pH* of a BOH solution?
4. How does dilution affect the *pH* of a solution of a weak acid?
5. How does the addition of NaAc affect the *pH* of an HCl solution?
6. How does the addition of Na_2PO_4 affect the *pH* of a dilute NaOH solution? A dilute HCl solution?
7. What happens when 100 ml of 0.100 *M* HCl are added to 100 ml of 0.100 *M* NaCN ? Repeat the explanation for (a) HAc and NaCN , (b) HBO_2 and NaCN .

Section 17E

1. What determines the pH of a buffer solution?
2. Explain how a solution of NaHCO_3 may act either as an acid or as a base. What other salts would show such action? Can a solution of NaHCO_3 properly be called a buffer?
3. Choose a buffer system other than the ones in Table 17.3 (p. 324) that would be suitable for a pH around 4.0.
4. Why would an HAc-NaAc system not be a good buffer for the pH region around 3.5?
5. Which has the higher buffer capacity, 0.10 M HAc —0.20 M NaAc , or 0.30 M HAc —0.30 M NaAc ? Which has the higher pH ?
6. Explain why glycine can be used as a buffer component in either an acid system or a basic system (Table 17.3).
7. Tris (hydroxymethyl) aminomethane is commonly used in buffers. Write the equation for its ionization. Give the pH range in which its buffering action is most effective.
8. Prideaux and Ward universal buffer consists of an equimolar mixture of three acids: H_3PO_4 , phenylacetic, and boric (**P9**). To prepare a buffer solution at a particular pH in the region 2–12, it is simply neutralized to the desired pH with NaOH . Explain why the pH shows no inflections and increases almost linearly with the amount of alkali added.
9. Compare the relative stabilities in air of pH 4 and pH 8 buffers.

Section 17F

1. Write equations for the acid ionization of benzoic acid ($\text{C}_6\text{H}_5\cdot\text{COOH}$), and for the basic ionization of sodium benzoate. Which of these occurs more extensively? Which is classed as a hydrolysis?
2. Repeat Ques. 1 for the acid ionization of Na_2HPO_4 and the basic ionization of Na_3PO_4 .
3. Repeat Ques. 1 for the acid ionization of phenol ($\text{C}_6\text{H}_5\text{OH}$) and the basic ionization of sodium phenolate ($\text{C}_6\text{H}_5\text{ONa}$).
4. Write equations for the basic ionization of aniline ($\text{C}_6\text{H}_5\cdot\text{NH}_2$) and the acid ionization of aniline hydrochloride ($\text{C}_6\text{H}_5\cdot\text{NH}_3\text{Cl}$). Which of these occurs more extensively? Which is classed as a hydrolysis?
5. Repeat Ques. 4 for the basic ionization of trimethylamine, $(\text{CH}_3)_3\text{N}$, and the acid ionization of trimethylamine hydrochloride, $(\text{CH}_3)_3\text{NHCl}$.
6. Explain how a salt may hydrolyze inappreciably, and yet greatly change the pH of the water in which the salt is dissolved.
7. Is an aqueous solution of each of the following salts acid, basic, or neutral? NaCl , Na_2CO_3 , NH_4Cl , NH_4CN , Na_3PO_4 , $(\text{NH}_4)_2\text{C}_2\text{O}_4$, NH_4BO_2 , $\text{NH}_2\text{OH}\cdot\text{HCl}$, $\text{C}_6\text{H}_5\text{ONa}$.
8. Boiling a solution of pure Na_2CO_3 for a few hours increases the pH and decreases the carbonate content. Describe this decomposition, using ionic equations.
9. Decide whether the first solution of each of the following pairs has a pH higher than, lower than, or practically identical with the pH of the second solution. (a) 0.10 M HAc —0.20 M HAc . (b) 0.10 M HAc —0.10 M benzoic acid. (c) 0.10 M NH_3 —0.10 M NH_4Cl ; 0.10 M NH_3 . (d) 0.10 M NaHCO_3 —0.10 M Na_2CO_3 . (e) 0.10 M NaAc —0.10 M NH_4Cl . (f) 0.10 M NaAc —0.10 M NaBO_2 . (g) 0.10 M NaAc —0.20 M NaAc . (h) 0.010 M NaOH —0.010 M NaOH ; 0.010 M NaAc .

(i) 0.10 *M* H₂SO₄—0.20 *M* HCl. (j) 0.10 *M* NaHSO₄—0.10 *M* NaHCO₃. (k) 0.10 *M* NaOH—0.10 *M* NH₃.

10. The following equilibrium is used to describe the behavior of an NH₄CN solution:



If this were the only equilibrium, what would be the *pH* of the NH₄CN solution? What additional equilibria must be considered in order to deduce the *pH*?

Sections 17H, I

1. Write chemical equations and ionization-constant expressions for the stepwise ionizations of the following polyprotic acids: sulfurous, silicic, citric, mercaptoacetic, glycine hydrochloride (HOOC·CH₂·NH₃Cl).

2. Repeat Ques. 1 for the following polyequivalent bases: hydrazine, ethylenediamine, sodium glycinate (NH₂·CH₂·COONa).

3. Write equations for the acid ionization of all of the acid forms of tyrosine. Repeat for the basic ionization of all of the basic forms of tyrosine. Which forms are amphiprotic?

4. Na₂HPO₄ is called an "acid salt." Explain why it is more appropriate to call this substance a base rather than an acid.

5. Inspection of the compounds in Appendix VIIB indicates that *pK_a* for a carboxylic group is around 5, while that for a phenolic group is around 10. Compare the basic strengths of the amino (—NH₂) and pyridine (C₅H₅N) groups. Use these comparisons to explain why 8-hydroxyquinoline does not exist in zwitter-ion form.

PROBLEMS

Section 17B

1. How many times is *K_w* increased in going from 25°C to 100°C? How many times is the percentage ionization increased? *Ans.* 51; 7.1.

2. From *K_w* = [H₃O⁺][OH[−]], derive the relationship *pK_w* = *pH* + *pOH*.

3. Find [H₃O⁺], [OH[−]], *pH*, and *pOH* for each of the following solutions: (a) 0.00135 *M* HCl; (b) 0.00035 *M* NaOH; (c) 0.0012 *M* Ba(OH)₂; (d) a solution of *pH* 4.87; (e) a solution of *pOH* 9.76; (f) 2.50 *M* HCl; (g) 1.95 *M* NaOH.

Ans. (a) [H₃O⁺] = 0.00135 *M*, *pH* = 2.87,

pOH = 11.13, [OH[−]] = 7.5 × 10^{−12} *M*.

4. What volume of 0.10 *M* HCl must be added to 100 ml of pure water (*pH* = 7) to lower the *pH* to (a) 5.00, (b) 4.00, (c) 3.00, (d) 2.00, (e) 1.00? *Ans.* (b) 0.10 ml.

5. What is the *pH* of pure water at 100°C? Explain why Table 17.2 (p. 318) is not valid at this temperature. *Ans.* 6.14.

6. Graph the relationship between *pH* and *pOH* at (a) 25°C, (b) 100°C. Use the same graph for both plots.

7. Sorenson's *pH* scale was proposed around 1909, and is most widely accepted today. However, other scales have been proposed. Giribaldo's rational scale defines a unit, *pR*, that increases with acidity: *pR* = log [H₃O⁺]/[OH[−]]. Add a column of *pR* values to Table 17.2. Reasons for the widespread acceptance of *pH* over other units are given by Bates (B5, Chap. 2).

8. What is the *pH* of a solution prepared by mixing 20.0 ml of 0.100 *M* HCl, 17.6 ml of 0.089 *M* NaOH, and 25.0 ml water?

Sections 17C, D

1. A 0.200 *M* solution of HA has a pH of 4.87. Calculate K_a .
Ans. 9.1×10^{-10} .
2. A solution that is 0.192 *M* in HA and 0.163 *M* in NaA has a pH of 6.87. Calculate K_a .
3. A 0.150 *M* solution of a base, B, has a pH of 10.53. Calculate K_b .
Ans. 7.7×10^{-7} .
4. Calculate the pH in the following solutions: (a) 0.100 *M* formic acid; (b) 0.050 *M* benzoic acid and 0.150 *M* sodium benzoate; (c) 0.0130 *M* NH_3 ; (d) 0.100 *M* aniline; (e) 0.100 *M* NH_3 and 0.200 *M* NH_4Cl .
Ans. (a) 2.39.
5. Calculate the pH in the solutions formed by mixing 25.0 ml of 0.100 *M* acetic acid with: (a) 35.0 ml water; (b) 40.0 ml of 0.150 *M* NaAc; (c) 25.0 ml of 0.072 *M* NaOH; (d) 10.0 ml of 0.100 *M* HCl plus 20.0 ml of 0.085 *M* NaAc; (e) 10.0 ml of 0.100 *M* HCl.
Ans. (b) 5.14.
6. Calculate the pH in the solutions formed by mixing 25.0 ml of 0.100 *M* ethanolamine with: (a) 25.0 ml water; (b) 20.0 ml of 0.080 *M* ethanolamine hydrochloride; (c) 30.0 ml of 0.065 *M* HCl; (d) 35.0 ml of 0.100 *M* NaOH.
Ans. (c) 9.05.
7. What is the pH when 45.0 ml of 0.100 *M* HCl are mixed with 45.0 ml of 0.100 *M* NaCN and enough water to give 100 ml?
Ans. 5.28.
8. Calculate the final pH and the change in pH when each of the following solutions is diluted one hundredfold: (a) an HCl solution of pH 2.00; (b) an HCl solution of pH 6.00; (c) a 0.060 *M* HCl solution; (d) a 0.060 *M* HAc solution; (e) an HAc solution of pH 2.80.
Ans. (d) 4.02, 1.03.
9. What volume of each of the following solutions must be diluted with water to give one liter of solution with a pH of 10.86? (a) 0.0100 *M* KOH, (b) 1.00 *M* NH_3 .
Ans. (b) 29 ml.
10. A solution contains 0.065 *M* NH_3 . To what concentration must it be diluted to quadruple the percentage ionization?
11. A solution is *C* *M* in HA. (a) Derive an expression for $[\text{H}_3\text{O}^+]$ in terms of *C* and K_a . (b) Simplify the expression for the case that $[\text{H}_3\text{O}^+] \ll C$.
Ans. (a) $(\sqrt{K_a^2 + 4K_aC} - K_a)/2$; (b) $[\text{H}_3\text{O}^+] = \sqrt{K_aC}$.
12. A solution is C_a *M* in HA and C_s *M* in NaA. (a) Derive an expression for $[\text{H}_3\text{O}^+]$ in terms of C_a , C_s , and K_a . (b) Simplify the expression for the case that $[\text{H}_3\text{O}^+] \ll C_a$, C_s .
Ans. (b) $[\text{H}_3\text{O}^+] = K_a C_a / C_s$.
13. A solution is C_b *M* in the weak base, B, and C_s *M* in its salt, BHCl. (a) Derive an expression for $[\text{OH}^-]$ in terms of C_b , C_s , and K_b . (b) Simplify the expression for the case that $[\text{OH}^-] \ll C_b$, C_s .
Ans. (b) $[\text{OH}^-] = K_b C_b / C_s$, or $[\text{H}_3\text{O}^+] = K_a C_s / (K_b C_b)$.
14. Give a general expression for the percentage ionization (*P*) of *C* *M* B.

Section 17E

1. In what molar proportions must HAc and NaAc be mixed to give a buffer of pH 4.90?
Ans. HAc:NaAc = 0.72.
2. In what molar proportions must NH_3 and NH_4Cl be mixed to give a buffer of pH 9.30?
3. What is the pH of a buffer prepared from 3.0 mmoles of sodium formate and 6.0 mmoles of formic acid, diluted to 85 ml?
Ans. 3.47.
4. Describe the preparation of buffer solutions having the following pH values: 4.00, 5.00, 6.00, 7.00, 8.00, 9.00, 10.00.
Ans. For pH 6.00, use 0.020 *M* KH phthalate and 0.080 *M* K_2 phthalate.

5. Consider the two buffers: (a) 0.050 *M* NaAc, 0.150 *M* HAc, and (b) 0.150 *M* NaAc, 0.050 *M* HAc. Calculate the percentage change in $[H_3O^+]$ when each of these buffers is made 0.010 *M* in NaOH, and compare the answers with that of Ex. 1, page 322. Do the answers support the statement that buffering capacity is a maximum when $[HAc]/[Ac^-]$ is unity? *Ans.* (a) 22%; (b) 25%; yes.

6. How might a buffer of pH 5.45 be prepared from 0.100 *M* HAc and 0.100 *M* NaAc solutions?

7. A solution contains 0.0200 *M* NH_3 . To what concentration must solid NH_4Cl be added to decrease the pH by one unit? Assume that the addition of NH_4Cl does not change the volume of the solution significantly. *Ans.* 0.0061 *M*.

8. How many grams of solid benzoic acid must be added to 100 ml of 0.090 *M* NaOH to give a pH of 4.60? (Assume that the volume of solution is not changed by addition of the solid.)

9. (a) How many moles of solid NaAc must be added to 100 ml of 0.090 *M* HAc to give a buffer of pH 5.20? (b) What is the pH change after the addition of 5.0 mmoles of solid NaOH to this buffer solution? (c) What is the pH change after the addition of 5.0 more mmoles of NaOH? Assume that the solids cause no volume changes in the solutions.

Ans. (a) 0.0251 moles; (b) 0.43 pH units; (c) 6.80 pH units.

10. A buffer solution contains 0.100 *M* benzoic acid and 0.100 *M* sodium benzoate. What volume of this buffer solution will undergo a change of one pH unit when 50 ml of 0.050 *M* H_2SO_4 are added?

Section 17F

1. Calculate the pH of the following solutions: (a) 0.050 *M* NaAc; (b) 0.200 *M* NaCN; (c) 0.100 *M* NH_4Cl ; (d) 0.0300 *M* aniline hydrochloride. *Ans.* (b) 11.26.

2. A solution containing 0.100 *M* NaX has a pH of 10.00. What is K_a for the acid HX? What is K_b for the base X^- ?

3. A 0.100 *M* BCl solution has a pH of 4.90. What is K_a for the acid B^+ ? What is K_b for the base BOH? *Ans.* $K_a = 1.58 \times 10^{-9}$; $K_b = 6.3 \times 10^{-6}$.

4. How many moles per liter of each of the following solutes must be dissolved to give a solution of pH 10.50? (a) KOH, (b) NH_3 , (c) $NaBO_2$.

5. What is the pH of a solution containing 0.100 *M* NaAc and 0.00100 *M* NaOH? *Ans.* 11.00.

6. Calculate the pH of 0.100 *M* phenol. If 100 ml of 0.100 *M* phenol are exactly "neutralized" with 100 ml of 0.100 *M* NaOH, what is the pH of the resulting solution? Is it proper to refer to sodium phenolate as a moderately strong base?

Section 17G

1. What is the pH in: (a) 0.00010 *M* H_2O_2 ; (b) 1.0×10^{-8} *M* hydroxylamine; (c) 1.0×10^{-6} *M* NH_4Cl ? *Ans.* (a) 6.99.

2. What is the pH in: (a) 0.100 *M* NH_4CN ; (b) 0.100 *M* NH_4Ac ?

3. Calculate $[H_3O^+]$ and the concentrations of the other solute species in each of the following solutions: (a) 0.00100 *M* HAc, 0.0100 *M* HBO_2 ; (b) 0.100 *M* HAc, 0.0100 *M* HOCl; (c) 0.050 *M* HOCN, 0.020 *M* HAc; (d) 0.0100 *M* NH_3 , 0.0100 *M* aniline; (e) 0.100 *M* ethylamine, 0.100 *M* tris (hydroxymethyl) aminomethane.

Ans. (b) $[H_3O^+] = 0.00132$ *M*, $[HAc] = 0.099$ *M*, $[HOCl] = 0.0100$ *M*, $[Ac^-] = 0.00132$ *M*, $[OCl^-] = 2.4 \times 10^{-7}$ *M*.

4. Calculate $[H_3O^+]$ and the concentrations of the other solute species in each of the following solutions: (a) 0.100 *M* sodium benzoate, 0.0100 *M* sodium phenolate;

(b) 0.100 *M* aniline hydrochloride, 0.100 *M* phenol; (c) 0.050 *M* chloroacetic acid, 0.050 *M* ethanolamine hydrochloride.

Ans. (b) $[\text{H}_3\text{O}^+] = [\text{C}_6\text{H}_5\cdot\text{NH}_2] = 0.00153 \text{ M}$,
 $[\text{C}_6\text{H}_5\cdot\text{NH}_3^+] = 0.098 \text{ M}$, $[\text{C}_6\text{H}_5\text{OH}] = 0.100 \text{ M}$, $[\text{C}_6\text{H}_5\text{O}^-] = 6.9 \times 10^{-9} \text{ M}$.

5. A solution contains 0.0100 *M* MgCl_2 and 0.0100 *M* FeCl_3 . (a) Give the *pH* range within which the solution must be adjusted so that no $\text{Mg}(\text{OH})_2$ precipitates, and less than 1.0% of the Fe^{3+} remains in solution. (b) Formulate a buffer solution in which the above separation might be performed, and calculate the percentage of Fe^{3+} that remains in solution.

Ans. (a) 2.84–9.52.

Section 17H

1. Calculate the concentrations of the various species in 0.100 *M* H_2SO_4 .

Ans. $[\text{H}_3\text{O}^+] = 0.109 \text{ M}$, $[\text{HSO}_4^-] = 0.091 \text{ M}$, $[\text{SO}_4^{2-}] = 0.0086 \text{ M}$.

2. Calculate the concentrations of the various solute species in: (a) 0.0100 *M* H_2CO_3 and 0.0100 *M* HCl ; (b) 0.0100 *M* H_2CO_3 ; (c) pure water saturated with CO_2 at a pressure of one atmosphere.

3. SO_2 is passed through water until the partial pressure of SO_2 above the solution is 0.0100 atm. Calculate the concentrations of the various solute species in the solution.

Ans. $[\text{H}_2\text{SO}_3] = 0.0123 \text{ M}$,
 $[\text{H}_3\text{O}^+] = [\text{HSO}_3^-] = 0.0146 \text{ M}$, $[\text{SO}_3^{2-}] = 6.3 \times 10^{-8} \text{ M}$.

4. Calculate the concentrations of the various solute species in an aqueous solution that is saturated with H_2S at one atmosphere.

5. Calculate the *pH* of 0.100 *M* NaH_2AsO_4 .

Ans. 4.60.

6. Calculate the *pH* of a solution containing 0.100 mole of ethylenediamine and 0.140 mole of HCl per liter.

7. What weight of NaHC_2O_4 must be added to 100 ml of 0.100 *M* $\text{Na}_2\text{C}_2\text{O}_4$ to give a buffer of *pH* 4.50?

Ans. 0.57 g.

8. Calculate the concentrations of the various solute species at *pH* 12.00 in the system of Fig. 17.1 (p. 334).

Section 17I

1. Calculate the fraction of a weak monoprotic acid that exists in the salt form when the acid is put into systems buffered at the following *pH*'s: $pK_a - 2$, $pK_a - 1$, pK_a , $pK_a + 1$, $pK_a + 2$.

Ans. 1.0%, 9.0 (approx. 10)%,
 50%, 91 (approx. 90)%, 99%.

2. What are the concentrations of the various solute species in a 0.0100 *M* glycine solution buffered at *pH* (a) 3.00, (b) 9.00, (c) 11.00?

3. What is the *pH* of a solution containing 0.100 *M* glycine and (a) 0.035 *M* HCl , (b) 0.035 *M* NaOH ?

Ans. (a) 2.65.

4. Calculate the concentrations of the various solute species in 0.0100 *M* 8-hydroxyquinoline buffered at the following *pH* values: 4.00, 5.00, 6.00, 7.00, 8.00, 9.00, 10.00, 11.00, 12.00. Prepare a graph like that of Fig. 17.1.

5. What is the *pH* of a solution containing 0.100 *M* 8-hydroxyquinoline and 0.015 *M* HCl ?

Ans. 5.73.

6. What is the *pH* in a solution containing 0.050 *M* piperazine and 0.080 *M* HCl ?

18 ACID-BASE TITRATIONS

18A. TITRATION CURVES

18A.1. The Course of a Titration

To find the equivalents of an acid (HA) in a sample, an indicator is added and the solution is titrated with standard NaOH. Before the equivalence point, HA is in excess and the indicator shows its characteristic acid color. As NaOH is added, HA reacts to form NaA, until all the acid is finally converted to NaA at the equivalence point. The diminution in HA concentration and the build-up of NaA and NaOH concentrations are depicted in the strip graphs at the top of Fig. 18.1.

As soon as the first slight excess of NaOH is added past the equivalence point, the solution becomes basic and the indicator assumes its characteristic basic color. It may be seen, therefore, that the sought-for equivalence point is bracketed by the transition of the indicator from an acid color to a different, basic color. Measurement of the volume of standard NaOH required to reach this transition point allows calculation of the equivalents of NaOH used in the titration; the equivalents of base so calculated will be the same as the sought-for equivalents of acid in the sample.

Figure 18.1 also shows the pH change during the titration as a function of volume of standard NaOH added. With the aid of Fig. 18.1, the student should correlate the changes in pH , composition, and indicator color to obtain a semiquantitative feeling for the titration process. In the following sections, the titration process is studied more quanti-

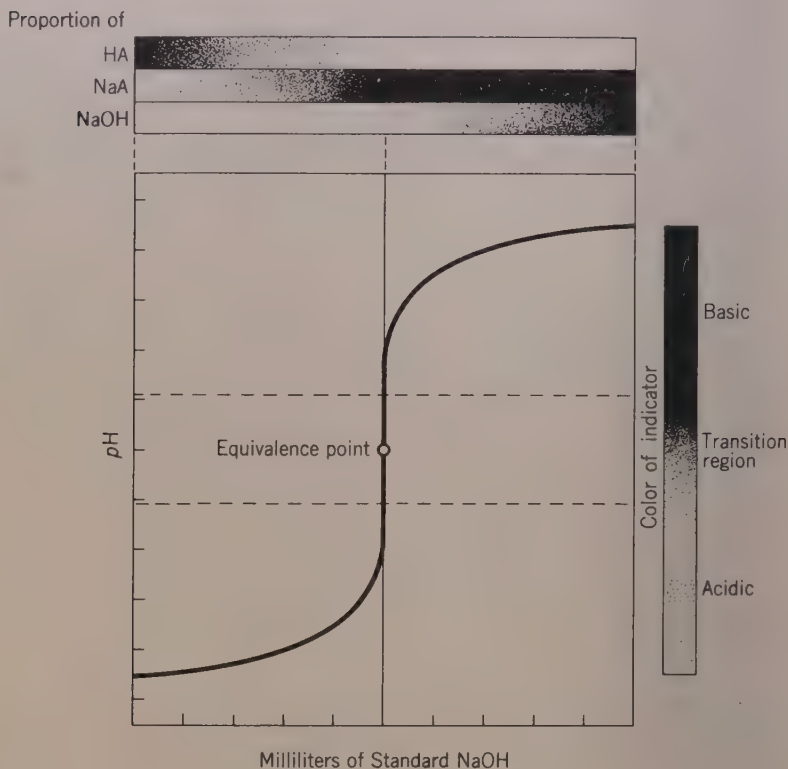


FIG. 18.1. Titration of an Acid with Standard NaOH

tatively, and application of this study is made to the practical performance of titrations, selection of indicators, and estimation of end-point errors.

18A.2. Titration Curve for a Monoprotic Acid

To explain the processes that occur in titration, it is desirable to calculate titration curves. Figure 18.2 gives a series of such calculated titration curves for monoprotic acids of different strengths. Figure 18.3 is a hundredfold horizontal enlargement of Fig. 18.2, showing more clearly the changes occurring near the equivalence point. The construction of these curves is explained below.

18A.2a. Titration of a strong acid with a strong base. In titrating a strong acid (e.g., HCl) with a strong base (e.g., NaOH), the only important equilibrium is



$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$$

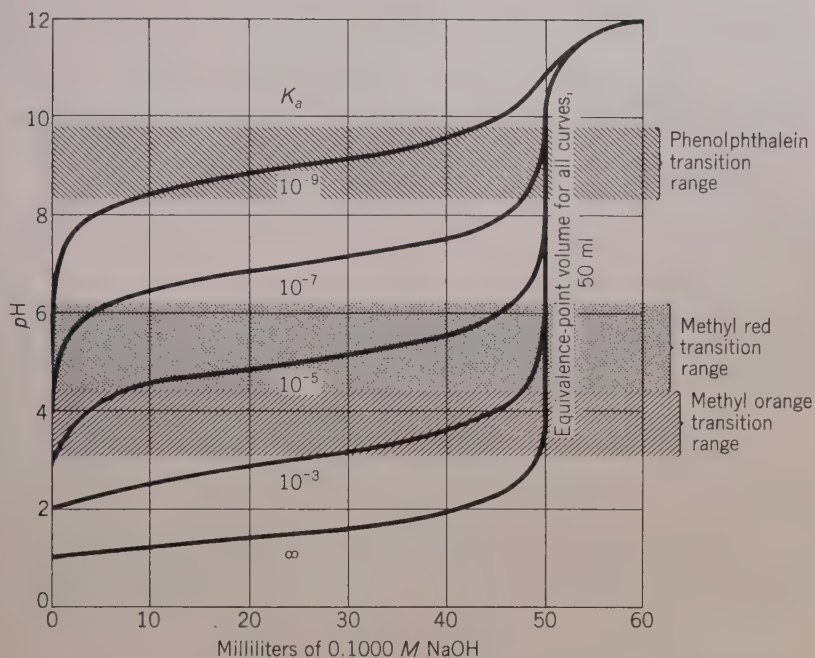


FIG. 18.2. Titration of HA with NaOH—Conditions: 50.00 ml of 0.1000 M HA titrated with 0.1000 M NaOH. $K_w = 1.00 \times 10^{-14}$. Activity effects disregarded. Volumes assumed additive.

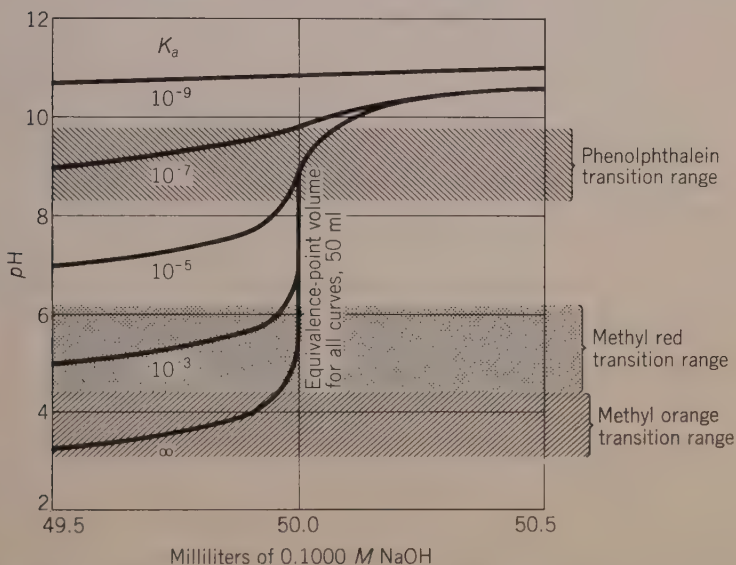


FIG. 18.3. Titration of HA with NaOH—Conditions: 50.00 ml of 0.1000 M HA titrated with 0.1000 M NaOH. $K_w = 1.00 \times 10^{-14}$. Activity effects disregarded. Volumes assumed additive.

At all points in the titration, $[\text{H}_3\text{O}^+]$ and $[\text{OH}^-]$ are determined by this equilibrium and by the excess of acid or base present, as shown in the following example. The curves labeled K_∞ in Figs. 18.2 and 18.3 are for strong acid–strong base titrations.

Example. Calculate the $p\text{H}$ when 49.00 ml of 0.1000 M NaOH are added to 50.00 ml of 0.1000 M HCl.

There are 49.00×0.1000 , or 4.900 meq of NaOH, and 50.00×0.1000 , or 5.000 meq of HCl. These react mole for mole, leaving an excess of 0.100 meq of HCl in a volume of $50.00 + 49.00$, or 99.00 ml. The HCl concentration is therefore $0.100/99.00$, or 0.00101 M . Since HCl is completely ionized, $[\text{H}_3\text{O}^+]$ is also 0.00101 M .

$$p\text{H} = -\log [\text{H}_3\text{O}^+] = -\log 0.00101 = 3.00$$

Other points on the curve may be similarly calculated. After the equivalence point, the excess of base determines $[\text{OH}^-]$, from which $[\text{H}_3\text{O}^+]$ may be calculated. In the region of the equivalence point ($p\text{H}$ 6–8), the computational methods on pages 769–74 must be used. However, points in the $p\text{H}$ 6–8 region need not be computed in order to delineate the curve, since it is so steep for a strong acid–strong base titration.

18A.2b. Titration of a weak acid with a strong base. At any point in the titration, the $p\text{H}$ may be calculated from the composition of the titrated solution by the methods of Chapter 17. Up to the equivalence point, the solution contains only HA and NaA, and the $p\text{H}$ may be calculated from the (acid) ionization constant of HA. At the equivalence point, the solution contains only NaA, and the $p\text{H}$ may be calculated from the (basic) ionization constant of A^- . After the equivalence point, the basic ionization (i.e., hydrolysis) of A^- is repressed by the excess of NaOH, and $[\text{OH}^-]$ is determined principally by the excess of NaOH.

Walton derives a general equation for the titration curve (i.e., $[\text{H}_3\text{O}^+]$ as a function of K_a , K_w , and composition) (W5). However, the equation is a quartic, and the less general methods used in the following examples are advocated for calculating points on the titration curve.

Example 1. What is the $p\text{H}$ in the titration of HA ($K_a = 1.00 \times 10^{-5}$) when 30.00 ml NaOH are added under the conditions of Fig. 18.2?

Originally, there are 50.00×0.1000 , or 5.000 meq of HA. The NaOH added (30.00×0.1000 , or 3.000 meq) reacts mole for mole with the HA, forming 3.000 meq of NaA, and leaving $5.000 - 3.000$, or 2.000 meq of HA, all in a total volume of $50.00 + 30.00$, or 80.00 ml. The molarity of NaA is $3.000/80.00$, or 0.03750 M , and the molarity of the HA is $2.00/80.00$, or 0.02500 M .

Since the solution contains the weak acid and its salt,



Letting $[\text{H}_3\text{O}^+] = x$, the concentrations of the other solute species are $[\text{A}^-] = 0.03750 + x$ and $[\text{HA}] = 0.02500 - x$. Substituting these concentrations into the ionization-constant expression, we obtain

$$\frac{x(0.03750 + x)}{(0.02500 - x)} = 1.00 \times 10^{-5}$$

$$x, \text{ or } [\text{H}_3\text{O}^+] = 6.7 \times 10^{-6} M$$

$$p\text{H} = -\log [\text{H}_3\text{O}^+] = -\log (6.7 \times 10^{-6}) = 5.18$$

Example 2. Calculate the $p\text{H}$ at the equivalence point in the titration of HA ($K_a = 1.00 \times 10^{-5}$) with NaOH under the conditions of Fig. 18.3.

At the equivalence point, when 50.00 ml of 0.1000 M NaOH are added to 50.00 ml of 0.1000 M HA , neutralization takes place to form 0.0500 M NaA . The NaA is a weak base. ($K_b = K_w/K_a = 1.00 \times 10^{-14}/1.00 \times 10^{-5}$, or 1.00×10^{-9} .)



If $[\text{OH}^-] = x$, $[\text{HA}]$ is also x , and $[\text{A}^-]$ is $0.0500 - x$. Substituting these concentrations into the ionization-constant expression, we have

$$1.00 \times 10^{-9} = \frac{(x)(x)}{0.0500 - x}$$

$$x, \text{ or } [\text{OH}^-] = 7.07 \times 10^{-6} M$$

$$p\text{OH} = 5.15; p\text{H} = 8.85$$

Example 3. What is the $p\text{H}$ in the titration of HA ($K_a = 1.00 \times 10^{-5}$) when 50.10 ml of NaOH are added under the conditions of Fig. 18.3?

The original 5.000 meq of HA will react mole for mole with the added NaOH (50.10×0.1000 , or 5.010 meq), forming 5.000 meq of NaA and leaving 0.010 meq of excess NaOH , all in a volume of $50.00 + 50.10$, or 100.10 ml. The molarity of the NaA is therefore $5.000/100.10$, or 0.04995 M , while the molarity of the excess NaOH is $0.010/100.10$, or 0.00010 M .

As a first approximation, it may be assumed that $[\text{OH}^-]$ is significantly contributed to only by the excess NaOH , so that $[\text{OH}^-] = 0.00010 M$, and $p\text{OH} = 4.00$.

After the manner of Ex. 2, the extent of hydrolysis (i.e., basic ionization) of A^- may be checked. Let y be the moles per liter of A^- hydrolyzed. Then $[\text{HA}] = y$, $[\text{OH}^-] = 0.00010 + y$, and $[\text{A}^-] = 0.04995 - y$. Substituting these concentrations into the basic ionization-constant expression for A^- ,

$$1.00 \times 10^{-9} = \frac{(y + 0.00010)y}{(0.04995 - y)}$$

$$y = 5 \times 10^{-7} M$$

The protolysis of A^- is indeed negligible (since $y \ll 0.00010$), and the estimate of 4.00 for $p\text{OH}$ is a good one. From $p\text{OH}$, the $p\text{H}$ may be calculated as 10.00.

Example 4. In making quick estimates of the shapes of titration curves, the following "landmark" approximations are useful. Their derivations are left as exercises for the student.

(a) At the beginning of the titration, when the solution contains only HA at a concentration C ,

$$[\text{H}_3\text{O}^+] = \sqrt{K_a C} \quad \text{or} \quad \text{pH} = \frac{1}{2}pK_a + \frac{1}{2}pC$$

(b) At the halfway point, when half of the acid has been neutralized, the HA and NaA concentrations are equal, and $[\text{H}_3\text{O}^+]$ is independent of concentration.

$$[\text{H}_3\text{O}^+] = K_a \quad \text{or} \quad \text{pH} = pK_a$$

(c) At the equivalence point, where only the salt (i.e., the weak base, A^- , with a basic ionization constant $K_b = K_w/K_a$) exists at a concentration C ,

$$[\text{OH}^-] = \sqrt{K_b C} \quad \text{or}$$

$$[\text{H}_3\text{O}^+] = \sqrt{K_a K_w / C} \quad \text{or} \quad \text{pH} = 7 + \frac{1}{2}pK_a - \frac{1}{2}pC$$

18A.2c. The slope of a titration curve. The steeper the curve in the region of the equivalence point, the more precisely it may be established. In order to select titration conditions for maximum precision, it is helpful to understand how the steepness of the curve depends upon these conditions.

Inspection of Fig. 18.3 shows that the slope increases with the strength of HA. When the acid is very weak, the inflection is very slight; and the end point cannot be precisely established. Of course, any factors

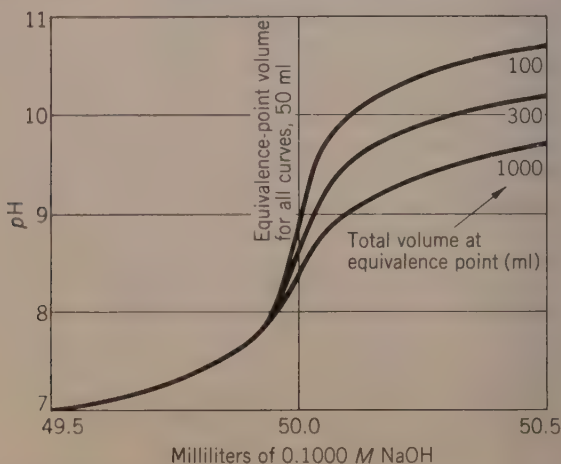


FIG. 18.4. Effect of Concentration on the Form of the Titration Curve—Conditions: 50.00 ml of 0.1000 M HA diluted with water, and then titrated with 0.1000 M NaOH. $K_w = 1.00 \times 10^{-14}$; $K_a = 1.00 \times 10^{-5}$. Activity effects disregarded. Volumes assumed additive.

affecting K_a also affect the steepness of the titration curve, but it should be noted that only relatively large changes in K_a affect the steepness of the titration curve significantly.

The volume in which the titration is carried out also affects the steepness of the titration curve. As shown in Fig. 18.4, the more dilute the solution, the less steep is the titration curve in the region of the equivalence point. It should be noted, however, that the steepest portion of the curve always comes at the equivalence point, regardless of the dilution. The curves of Fig. 18.4 are calculated in the same way as those of Fig. 18.3. Similar considerations show that the steepness decreases as the concentration of the standard base decreases.

It is worth noting that titration curves are not given for very weak acids ($pK_a < 9$). There are such acids (HPO_4^- , H_2O_2 , 8-hydroxyquinoline, NH_4^+ , etc.), but their titration is impracticable because they give almost no inflection. Such weak acids have strong conjugate bases, and the base forms are titratable with standard strong acid, as shown in the following section.

18A.3. Titration Curve for a Monoequivalent Base

Figure 18.5 shows the titration curves for a series of monoequivalent bases (B) of different strengths with a strong acid. These curves are computed in the same manner as those for Fig. 18.3. In fact, Fig.

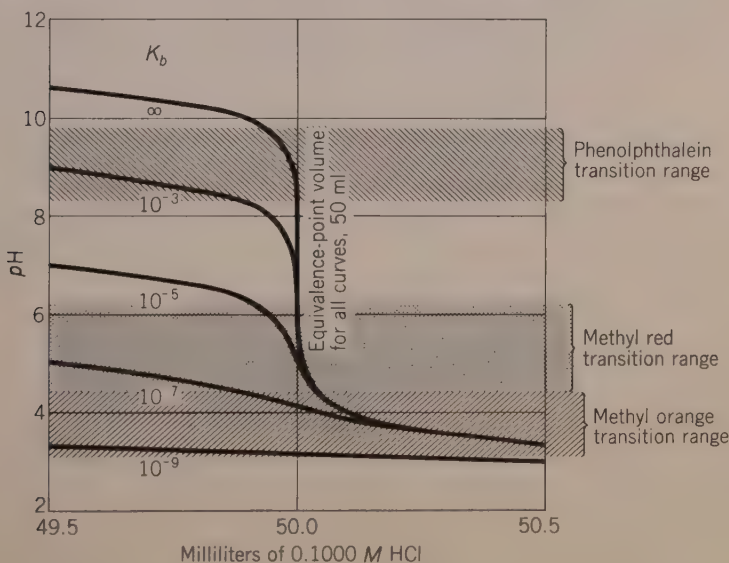


FIG. 18.5. Titration of B with HCl—Conditions: 50.00 ml of 0.1000 M B titrated with 0.1000 M HCl. $K_w = 1.00 \times 10^{-14}$. Activity effects disregarded. Volumes assumed additive.

18.5 is closely related to Fig. 18.3. It may be shown that the pOH curve for the titration of B with HCl is identical with the pH curve for the titration of HA with NaOH, provided that the ionization constants for B and HA are numerically equal.

18A.4. Titration of Salts

Salts of very weak acids are moderately strong bases. Thus, boric acid (HBO_2 , $pK_a = 9.19$) is too weak an acid to titrate accurately with NaOH. However, borates ($pK_b = 4.81$) are fairly strong bases and can be titrated accurately with standard HCl, as shown in Fig. 18.5.

Likewise, salts of very weak bases are rather strong acids, and can be accurately titrated with standard HCl, as shown in Fig. 18.3.

Points on titration curves of salts are calculated just as for other acids and bases. An example is given below. Other important examples are the titration of Na_2CO_3 with standard HCl (Exp. 18.1), and of NH_3 as NH_4BO_2 (Exp. 18.6).

Example. When the salt NaA ($K_b = 1.00 \times 10^{-5}$) is titrated with standard HCl under the conditions of Fig. 18.5, calculate the pH at the equivalence point.

When 50.00 ml of 0.1000 M HCl (5.000 meq) are added to the 50.00 ml of 0.1000 M NaA (5.000 meq), 5.000 meq of the conjugate acid HA are formed in a volume of 100.0 ml. The HA concentration is therefore 5.000/100.0, or 0.05000 M . If we let $[H_3O^+] = x$, then $[A^-] = x$, and $[HA] = 0.05000 - x$.

$$\frac{[H_3O^+][A^-]}{[HA]} = K_a = \frac{K_w}{K_b}$$

$$\frac{x^2}{0.05000 - x} = \frac{1.00 \times 10^{-14}}{1.00 \times 10^{-5}}$$

$$x, \text{ or } [H_3O^+] = 7.1 \times 10^{-6} M$$

$$pH = 5.85$$

18B. ESTABLISHING THE EQUIVALENCE POINT

18B.1. The pH Meter

The pH meter* is an instrument that measures the pH (really, pa_H) of a solution, and affords a direct method of obtaining the titration curve. The use of the pH meter in establishing the end point in acid-base titrations is described in the following two sections.

18B.1a. Selection of the inflection point. At several points in the region where pH changes sharply, the pH is measured and plotted as a

*The workings and theory of the pH meter cannot be properly presented until after redox theory has been studied.

function of volume of standard solution added. The best smoothed curve is drawn through these points. The steepest tangent is then drawn to the smoothed curve, and, within experimental error, this tangent coincides with the curve over a finite length. The end point is selected as the volume at the midpoint of this region of coincidence, which is the inflection point of the titration curve. The method is summarized in Fig. 18.6.

It was shown in preceding sections that the inflection point of a symmetrical titration curve is identical with the equivalence point, regardless of the conditions under which the titration is performed—that is, regardless of the concentration or strength of the acid or base being

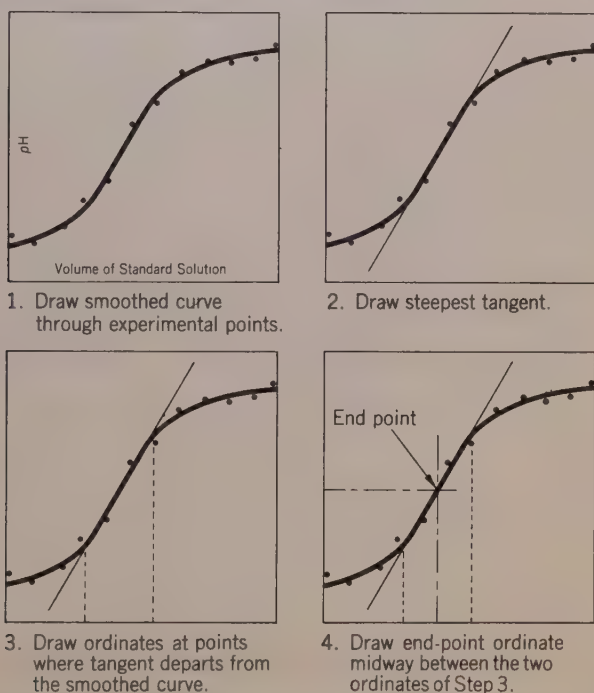


FIG. 18.6. Selection of the End Point from the Titration Curve

titrated, the ionic strength, or the actual pH at the equivalence point. The procedure of selecting the inflection point as the equivalence point is therefore more accurate than using indicators or titrating to a fixed pH . A disadvantage of using the inflection point is the time and effort required to make the measurements and to draw the titration curve. With modern instrumentation, however, this disadvantage is removed (see Supplement, p. 778).

18B.1b. Titration to a fixed pH. A faster but more restricted method is to select the end-point volume as that volume of standard solution required to reach a certain pH. The proper end-point pH may be determined experimentally on a known sample, or it may be calculated approximately from the ionization constants and concentrations of the solutes, as in Ex. 2, page 347. However, the equivalence-point pH is not invariant, but depends upon end-point volume and also upon variables affecting K_a or K_b , such as temperature and ionic strength. The equivalence-point pH may vary by several tenths of a pH unit from one titration to another, just owing to variation in sample size alone. However, if the titrated acid or base is reasonably strong, so that the titration curve is steep, then even a considerable difference between the chosen end-point pH and the true equivalence-point pH will cause only negligible error in the end-point volume, as shown in the following example. On the other hand, if the acid or base is quite weak, so that the titration curve is not steep, titration to a fixed pH may result in considerable error. For the titration of weak acids or bases, therefore, it is more accurate to select the inflection point than to titrate to a chosen pH.

Example. An end-point pH of 8.9 is chosen for the titration of HA ($K_a = 1.0 \times 10^{-6}$), in anticipation of the titration of samples under the conditions of Fig. 18.3. Suppose, however, that a 50.00-ml sample of 0.1000 M HA is diluted with water before titration, so that the equivalence-point volume is 300 ml instead of the anticipated 100 ml. What is the error of the titration?

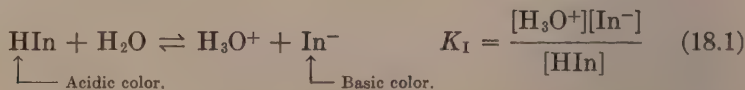
The correct equivalence-point volume is 50.00 ml of 0.100 M NaOH.

According to Fig. 18.4, titration to pH 8.9 requires 50.02 ml when the end-point volume is 300 ml.

The titration error is therefore $50.02 - 50.00$, or 0.02 ml, or 0.04%. This error is not significant, even though the equivalence-point pH (8.6, from Fig. 18.4) is appreciably different from the chosen end-point pH of 8.9.

18B.2. Acid-Base Indicators

18B.2a. Properties of indicators. An acid-base indicator is a weak organic acid.



The ionized and un-ionized forms of the indicator have different colors. (A more detailed description of the structure of indicators and the mechanism of the color change is given in the Supplement, p. 778.) When the indicator is put in acid solution, the equilibrium 18.1 is shifted predominantly to the left, the form HIn predominates, and the

solution shows the color of this form, which is called the acidic color of the indicator. In strongly basic solution, the form In^- predominates, and the color of this form is called the basic color of the indicator. If only one form of the indicator is colored, it is called a *one-color indicator*; if both forms are colored, it is called a *two-color indicator*.

If Eq. 18.1 is rearranged, we have

$$\frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{\text{I}}} \quad (18.2)$$

The color of the solution depends upon the ratio $[\text{HIn}]/[\text{In}^-]$, which in turn is dependent upon $[\text{H}_3\text{O}^+]$, as shown in Eq. 18.2. The color of the indicator solution may therefore be taken as a measure of $[\text{H}_3\text{O}^+]$ or pH .

The eye is not extremely sensitive to changes in hue. Thus for all solutions in which the ratio $[\text{HIn}]/[\text{In}^-]$ is below 1:10, the colors are not easily distinguishable from the pure basic color of In^- alone, and

$$[\text{H}_3\text{O}^+]_{\text{basic color}} \leq 0.1 K_{\text{I}} \quad (18.3a)$$

Similarly, for all solutions in which $[\text{HIn}]/[\text{In}^-]$ is above 10:1, the colors are not easily distinguishable from the pure acidic color of HIn alone, and

$$[\text{H}_3\text{O}^+]_{\text{acidic color}} \geq 10 K_{\text{I}} \quad (18.3b)$$

Converting Eqs. 18.3 to the logarithmic forms, we obtain

$$\left. \begin{aligned} (\text{pH})_{\text{basic color}} &\geq \text{p}K_{\text{I}} + 1 \\ (\text{pH})_{\text{acidic color}} &\leq \text{p}K_{\text{I}} - 1 \end{aligned} \right\} \quad (18.4)$$

For all pH values between the two limits of Eqs. 18.4, the colors of the indicator are intermediate between the pure acidic and pure basic colors, and may be taken as a measure of the pH . This pH range (i.e., $\text{p}K_{\text{I}} \pm 1$) is called the *transition range* of the indicator. It may be seen from Eqs. 18.4 that the transition ranges for all indicators extend over about 2 pH units, but that the actual location of the transition range on the pH scale depends on K_{I} , and varies from one indicator to another, falling at a pH of $\text{p}K_{\text{I}} \pm 1$. A chart of indicators, with transition ranges, is given in Appendix VIII (p. 928).

The above theory applies to two-color indicators that behave according to Eq. 18.1. However, there are indicators that deviate considerably from this behavior, which should therefore be regarded only as a rough general description of acid-base indicators. Some of the factors that affect the transition range are discussed in the Supplement (p. 779).

18B.2b. Selection of an indicator. The choice of an indicator to mark the equivalence point in a titration is governed by essentially the same

principles as those governing titration to a fixed pH . An indicator may be used most satisfactorily if the pH changes rapidly in the region of the equivalence point, so that the titration error is still small even if there is inadvertently a difference of a pH unit or so between the end point and the equivalence point. In other words, in passing from 0.1% before the equivalence point to 0.1% after, the pH should change by about 2 pH units. In such a case, it is necessary only to titrate uncritically to a *color change* of the indicator.

If the pH does not change very rapidly in the region of the equivalence point, it may still be possible to achieve good accuracy by titrating to a certain *color tint* of the indicator. The proper color tint may be determined by putting the indicator in a *comparison solution* having the same pH as exists at the equivalence point. The equivalence-point pH may be found: (1) By calculation, which is not very accurate. (2) By measuring the pH of a solution of the salt of the acid and base being titrated, using indicators or a pH meter. This is not always convenient because the salt may not be available in sufficient purity. (3) By measuring the inflection-point pH in the curve obtained by a pH titration of the sample. The comparison solution itself may be prepared by dissolving the salt of the acid and the base being titrated, or, if the salt is not available, a stable and permanent buffer solution of the proper pH may be prepared.

Titration to a certain color tint must be carefully controlled, for variations in conditions (sample size, end-point volume, temperature, and ionic strength) cause variance between the equivalence-point pH and the end-point pH . If such variations are important enough to affect the precision or accuracy desired, it is better not to use indicators, but to titrate to the inflection point with a pH meter. Walton discusses critically the effect of temperature and ionic strength on indicators (W5).

As far as indicator selection is concerned, the common acid-base titrations fall into four classes.

Strong acid with strong base. The pH change is so sharp and extends over so many pH units that many indicators may be used to establish the equivalence point well within 0.1% error. Thus, as shown in Fig. 18.3 (p. 345), the pH changes from 4 to 10 in passing from 0.2% before to 0.2% after the equivalence point. Phenolphthalein, methyl red, or methyl orange may be used in such titrations. The proper and most perceptible end points for these indicators are the first perceptible tinge of pink for phenolphthalein, and the disappearance of the last traces of red (giving a pure yellow) for methyl orange or methyl red.

Weak acid with strong base. The salt formed gives a basic reaction by hydrolysis, and an indicator with a transition range on the basic

side (such as phenolphthalein) should be used, as shown in Fig. 18.3. When phenolphthalein is used, the most frequent practice is to titrate to the first permanent trace of pink (pH about 8.3), rather than to a strong pink (pH 9–10). However, it is of interest to note that this procedure gives a premature end point in the titration of very weak acids. In such cases, it is necessary to titrate to a certain color tint of phenolphthalein, or to use an indicator with a more basic transition range. If the properties of the weak acid to be titrated are not known, it is best to titrate to the inflection point with a pH meter rather than to choose an indicator indiscriminately.

Weak base with strong acid. The salt formed gives an acid reaction by hydrolysis, and an indicator with a transition range on the acid side (such as methyl red) should be used, as shown in Fig. 18.5 (p. 349).

Weak base with weak acid, or vice versa. This case is not of practical interest, since it is always possible to choose a strong acid (or base) for the standard solution. Such a titration would not be precise, for the curve would not be at all steep in the region of the equivalence point. The salt of a weak acid and a weak base is really a buffer, which does not change appreciably in pH on the addition of acid or base.

Example. What would be the titration error if phenolphthalein were used as an indicator in the titration of HA ($K_a = 1.0 \times 10^{-7}$) under the conditions of Fig. 18.2?

Phenolphthalein begins to turn pink at pH 8.3. This pH is reached when about 47 ml of standard NaOH are added. Hence the end point is premature by about 3 ml, which corresponds to an error of 6%.

For this titration, it is better to use an indicator transiting in a more basic region, or to titrate to a certain color tint of phenolphthalein. An even better procedure would be to follow the titration to the inflection point with a pH meter.

18B.2c. Other kinds of indicators. *Mixed, fluorescent, and turbidity indicators* are described in the Supplement (p. 782). In some instances they may give greater accuracy than ordinary indicators.

18C. ERRORS IN ACID-BASE TITRATIONS

There are hosts of errors in acid-base titrations—errors associated with the operator, the facilities, and the titration method itself. These errors are too numerous and varied for brief systematic discussion, and they are best described under each method to which they apply.

However, there are three sources of potential error that are common to almost all acid-base titrations: (1) end-point error, (2) determinate error in the blank, (3) carbonate error. Properly handled, these errors can usually be made small; but they may become large if ignored.

18C.1. End-Point Error

18C.1a. Determinate error. If the titration is carried to the inflection point in a titration curve, there is no determinate error, for the inflection point coincides with the equivalence point. For indicator end points, there is such a great variety of indicators that one may always be chosen whose transition pH corresponds so closely with the equivalence-point pH that determinate error is negligible.

It is conceivable that in some cases, a titration might be carried to an end-point pH significantly different from the equivalence-point pH . The calculation of the end-point error in such a case is described in the Supplement (p. 783).

18C.1b. Random error in selecting the inflection point. In locating the inflection point, the standard error appears to be about 10% of the volume interval covered by the straight-line portion of the experimental titration curve. This figure of 10% is a rough estimate based on experience, and has no theoretical basis. Thus if the straight-line portion of the curve of Fig. 18.6 (p. 351) extended over a range of 0.3 ml, the standard error of estimating the equivalence point would be 0.03 ml, and errors in excess of 0.06 ml would not often be made. This error is purely random in nature for titration curves that are symmetrical about the equivalence point. For unsymmetrical curves, there may be some determinate error between the inflection point and the equivalence point, but this error is usually only a small fraction of the volume interval covered by the straight-line portion of the titration curve.

18C.1c. Random error of titrating to a certain pH . On page 352, it was shown that there may be a considerable difference (several tenths of a pH unit) between the chosen end-point pH and the true equivalence-point pH , especially when titration conditions are not closely controlled. For definiteness, let it be assumed that a standard deviation (i.e., standard error) of 0.5 pH unit may occur between the chosen end-point pH and the equivalence-point pH . In this case, the standard error of the end point is the volume of standard solution required to pass from the equivalence-point pH to a pH 0.5 unit greater (or less) than that at the equivalence point. Thus in the titration of HA ($K_a = 10^{-7}$) under the conditions of Fig. 18.3 (p. 345) the standard error is about 0.2 ml of 0.1 N base, or about 0.4%, relative.

The random error for a particular titration may be predicted in two ways. (1) The standard error of the end point may be estimated from the titration curve, which may be computed and plotted. This computation is laborious. Figures 18.2 to 18.5 and 18.9 (p. 362) give a sufficient number of titration curves so that the error for a particular titration may be estimated fairly well by comparison with the given curves.

Although such a comparison is not exact, it is sufficient for rough estimates of random end-point errors. (2) The pH is computed for the equivalence-point conditions, and then the volume of standard solution required to bring about a change of 0.5 pH unit is calculated. The method of calculation is given in the Supplement (p. 783).

Study of the preceding titration curves allows the following generalizations:

1. The standard end-point error is 0.1% or less in the titration of 0.1 N HA with 0.1 N NaOH, provided that K_a is about 10^{-6} or greater. The error rises to about 1% when K_a falls to 10^{-8} . The errors are similar for the titration of B with HCl.

2. The random end-point error increases with dilution (Fig. 18.4).

18C.2. Determinate Error in the Blank

The blank is the volume of standard acid (or base) required to neutralize any impurities in the water or reagents used to prepare the sample for titration. This includes the indicator blank. The determination of the blank is not so simple as may first be thought. The following example may make this clear.

Example. Suppose that a Na_2CO_3 -NaCl sample is dissolved in water, and a 50-ml aliquot is titrated with standard 0.10 N HCl to a methyl orange end point, which occurs at pH 4.0. The volume of standard HCl required is 49.65 ml. A blank determination is performed on a 100-ml portion of the water and the same amount of indicator as is used for the sample, and 0.12 ml of the standard acid is required. What, then, is the volume of standard HCl required to react with the Na_2CO_3 in the sample, corrected for the blank?

The experimental blank of 0.12 ml includes the amount of 0.10 N HCl required to take the water (exclusive of any impurities) from its neutral point of pH 7 to the end-point pH of 4. This is

$$(1.0 \times 10^{-4} - 1.0 \times 10^{-7}) \times \frac{100}{0.1000} = 0.10 \text{ ml}$$

In the titration of the Na_2CO_3 -NaCl sample, however, the solution at the end-point pH of 4 acquires its acidity not from any excess of standard HCl (as does the experimental blank determination), but rather from the ionization of the product, H_2CO_3 .

The experimental blank is therefore too large by 0.10 ml, and the correct value of the blank is only $0.12 - 0.10$, or 0.02 ml.

The volume of standard HCl required to titrate the sample is therefore $49.65 - 0.02 = 49.63$ ml. Use of the uncorrected experimental blank would cause an error of 0.10 ml, or 0.2%.

This correction to the experimental blank is significant only for end points that are appreciably removed from pH 7. For end points in the range of 5–9, the correction amounts to only 0.01 ml or less of 0.1 N standard solution per 100 ml of solution titrated, which may be neglected in ordinary titrations.

In any case, proper determination of the blank requires a knowledge of the end-point pH . Many workers prefer to neglect the blank entirely, keeping conditions in standardization and titration of the sample as similar as possible, so that compensation of errors may occur. A more reliable way to determine the blank correction is to titrate a precisely known amount of the sought-for substance with the standard solution, reckoning the blank as the difference between the theoretical and the experimental amounts required.

18C.3. The Carbonate (and Silicate) Error

It has been stated that HCl may be titrated with $NaOH$, either methyl orange or phenolphthalein being used, and that the choice of an end-point pH anywhere in the range of 4–10 causes only small errors. This is true only when the solutions contain no carbonate. It is very difficult to prepare and keep standard base solutions that are perfectly free of carbonate. Not only does reagent-grade $NaOH$ contain Na_2CO_3 , but $NaOH$ solutions avidly absorb CO_2 from the air. Student preparations of standard $NaOH$ often contain around 1 mole of Na_2CO_3 per 100 moles of $NaOH$.

Examination of Fig. 18.9 (p. 362) shows that the base normality of a solution containing Na_2CO_3 depends upon the end-point pH to which the solution is used. Thus, if a solution contains Na_2CO_3 in addition to $NaOH$, the normality of this solution as a base is less when used to the phenolphthalein end point (where CO_3^{2-} is converted to HCO_3^- and neutralizes only 1 mole of H_3O^+ per mole of CO_3^{2-}) than when used to the methyl orange end point (where CO_3^{2-} is neutralized to H_2CO_3 and neutralizes 2 moles of H_3O^+ per mole of CO_3^{2-}). If a solution contains 0.0990 M $NaOH$ and 0.0010 M Na_2CO_3 , its base normality is 0.1000 N to the phenolphthalein end point, but 0.1010 N to the methyl orange end point.

Therefore, from the practical standpoint it is important to specify the indicator (or end-point pH) employed in standardizing a base solution, and then to use the standard concentration value thus found only with this particular indicator (or end-point pH). If the standard base must be used to any other end-point pH , restandardization is necessary. This source of error is determinate, and may be eliminated by proper standardization and use of the base.

In addition, carbonate is an even more troublesome source of indeterminate error when the carbonate-containing base is used to titrate weak acids. Suppose that an $NaOH$ solution containing Na_2CO_3 is used to titrate an H_3PO_4 solution. The phenolphthalein end point is poor because neither the HCO_3^- end point (pH 8.3) nor the HPO_4^{2-}

end point ($pH\ 9.8$) is very sharp, and besides, they are $1.5\ pH$ units apart. The inflection in this region is therefore neither sharp nor symmetrical, and the end point is correspondingly in error. The methyl orange end point (CO_3^{2-} converted to H_2CO_3 ; H_3PO_4 converted to NaH_2PO_4) is similarly in error, but less so than the phenolphthalein end point because (1) the end points are sharper, and (2) the equivalence-point pH 's are closer together (only $0.5\ pH$ unit apart). It is for this reason that H_3PO_4 is best titrated as a monoprotic acid when the standard base contains carbonate as an impurity.

One obvious method of eliminating the carbonate error is to use carbonate-free base solutions, which may be prepared in several ways (**K19**). (1) The method of Exp. 18.1 takes advantage of the insolubility of Na_2CO_3 in concentrated $NaOH$, and gives base solutions containing only 1–2 moles of Na_2CO_3 per 1000 moles of $NaOH$. (2) $Ba(OH)_2$ may be used. Since $BaCO_3$ is insoluble, carbonate is completely precipitated. However, $Ba(OH)_2$ solutions are not convenient to work with; $BaCO_3$ precipitates on exposure to air, and films soon form on the container walls. Frequent restandardization is necessary. Also, a number of Ba salts are insoluble and may interfere in titrations. (3) Bright metallic Na may be dissolved in water, giving carbonate-free $NaOH$. (4) $NaOH$ may be prepared by electrolysis of an $NaCl$ solution. (5) $NaCl$ may be converted quantitatively (99.8%) to $NaOH$ by passage through a column containing a strong anion exchange resin. With simple precautions, the effluent solution is almost completely free of carbonate (**S27**).

However, no matter how completely CO_2 is eliminated, it may be reabsorbed from the air unless special precautions are taken in storage and use of the solution. Figure 18.7 depicts one of the many systems for storage and use of carbonate-free base. Other arrangements are described in the literature (**M2**, **M8**). For student use, the equipment of Fig. 18.7 is not practical. Instead, the $NaOH$ is stored in a bottle with a tightly fitting stopper, and used with minimum exposure to air. Since CO_2 is not rigidly excluded by these measures, it is necessary to standardize and use the solution so as to minimize the carbonate error, as described above.

$NaOH$ solutions stored in glass attack the glass, dissolving SiO_2 to form Na_2SiO_3 . Silicate in standard base solutions causes errors similar to carbonate, since silicic acid is very weak. Base solutions should be stored in bottles of borosilicate glass, which is more resistant than soft glass. Polyethylene bottles should not be used for storage, since they are permeable to CO_2 (**T1**).

The carbonate and silicate errors become relatively more important and difficult to eliminate as the concentration of the standard base de-

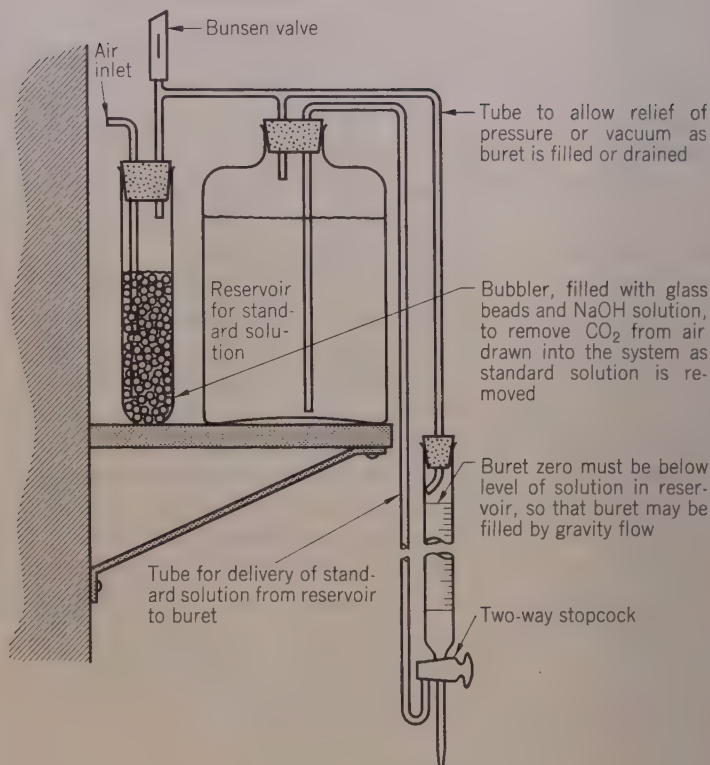


FIG. 18.7. Storage and Use of NaOH Solutions to Prevent Absorption of CO₂ from Air—The Bunsen valve is a short, longitudinal slit in a rubber policeman. This is a one-way valve, which allows escape of gas from the system to the atmosphere if excess pressure is built up in the system, but does not allow air from the atmosphere to enter the system, even if a slight vacuum develops therein. This arrangement of a bubbler and Bunsen valve is superior to a U-tube filled with NaOH pellets; the pellets absorb water from the standard solution, causing a change in concentration. The bubbler saturates the incoming air with water, preventing such a concentration change.

creases. Considerable pains are required to reduce these errors to the 0.1% level when 0.01 *N* base is used. Not only must CO₂ be kept out of solutions during storage, but air (with its CO₂) must be kept out of the titration vessel during the titration (c9).

18C.4. Reduction of Acid-Base Titration Errors

Much work has been done to improve the accuracy of marginal acid-base titrations. Some of the techniques are described in the Supplement (p. 784).

18D. TITRATION OF POLYPROTIC ACIDS

Equilibria involving polyprotic acids are described in Sec. 17H (p. 332).

18D.1. Titration Curves for Polyprotic Acids

Suppose that a mixture of two acids, HX and HY, is titrated with standard NaOH. If HX is much stronger than HY, the first portions of base react almost exclusively with HX, leaving HY unchanged. This process continues until virtually all HX is converted to NaX. Only when the HX equivalence point is passed will the added base begin to react with HY. If there is a great difference in acid strengths (i.e., if the ratio of the ionization constants is 10^4 or greater), the titration curve shows a sharp inflection at the HX equivalence point, and it is possible to titrate HX in the presence of HY (Fig. 18.8a). Also,

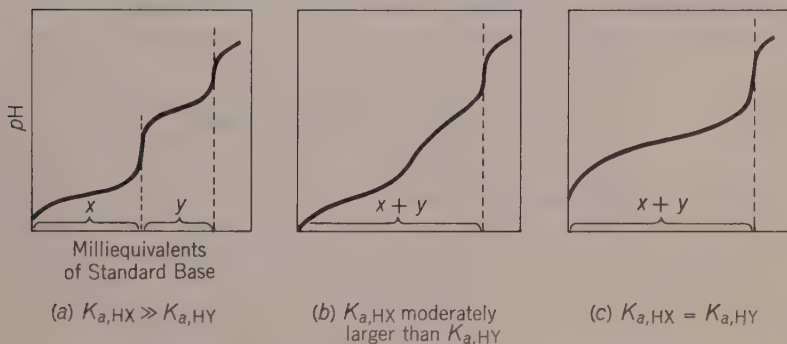


FIG. 18.8. Titration of a Mixture of Two Acids—Mixture contains x meq of HX and y meq of HY.

if HY is not too weak the titration may be continued to a perceptible end point for HY. If $K_{a,HX}$ is only moderately larger than $K_{a,HY}$, an appreciable portion of HY is converted to NaY at the HX equivalence point, and an appreciable portion of HX remains unneutralized. The steepness of the titration curve at the HX equivalence point is therefore reduced, and HX cannot be precisely titrated in the presence of HY (Fig. 18.8b). If HX and HY are of comparable strengths, the HX inflection point is obliterated (Fig. 18.8c). It may be shown that if the ratio of the ionization constants is 16 or less, there is no perceptible inflection at the equivalence point for HX (A15).

A strong acid may be titrated in the presence of an equimolar concentration of a weaker one with reasonable precision only if the ionization constant of the stronger acid is more than 10^4 -fold greater than

that of the weaker. Even then, the precision for the titration of the stronger acid is not as good as that obtainable by titrating a single acid of comparable strength, and the standard error of the end point appears to be several tenths of a per cent, using 0.1 *N* solutions. This error increases as the ratio of the ionization constants decreases, and when the ratio of the ionization constants becomes less than 1000, the stronger acid can no longer be precisely determined by direct titration in the presence of the weaker.

In titration, a polyprotic acid acts as a mixture of monoprotic acids, present in equimolar amounts. If the *K*'s are sufficiently different and not too small, there is an inflection point in the titration curve

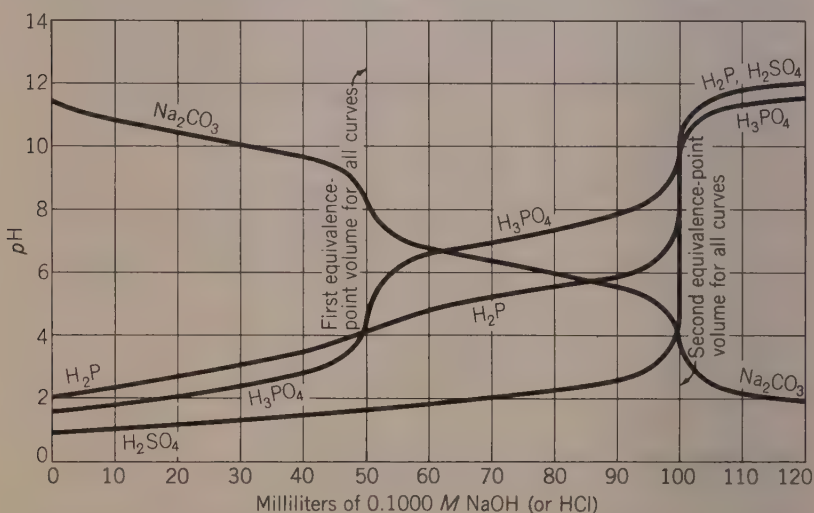


FIG. 18.9. Titration of Polyprotic Acids and Na_2CO_3 —Conditions: 50.00 ml of 0.1000 *M* acid (or Na_2CO_3) titrated with 0.1000 *M* NaOH (or HCl). Activity effects disregarded. Volumes assumed additive.

Ionization constants:

H_2SO_4	H_2P	H_3PO_4	H_2CO_3
∞	8.0×10^{-4}	7.1×10^{-3}	3.5×10^{-7}
1.0×10^{-2}	4.0×10^{-6}	6.2×10^{-8}	6.0×10^{-11}
		4.4×10^{-13}	

for each removable proton. If present alone in solution, a polyprotic acid may theoretically be determined by titration to any of these inflection points. In practice, however, not all these end points may be equally precise for a given acid, and some may not be perceptible at all. Polyequivalent bases behave similarly.

Figure 18.9 shows titration curves for H_2SO_4 , phthalic acid (H_2P), H_3PO_4 , and Na_2CO_3 . The individual titrations of these substances

are discussed below. The curves of Fig. 18.9 are constructed similarly to those of Figs. 18.1 to 18.5. Although elementary methods of computation suffice for some points on the curves, others must be computed more rigorously by the method of the principal equilibrium (p. 328), or by the methods in the Supplement (p. 769).

18D.2. Titrations of Polyprotic Acids and Na_2CO_3

H_2SO_4 . With respect to the first ionization step, H_2SO_4 is a strong acid, like HCl , and K_1 is infinitely large. HSO_4^- is also moderately strong, and there is no inflection whatever at the first equivalence point for H_2SO_4 . The inflection at the second equivalence point is steep and sharp; therefore, H_2SO_4 may be accurately titrated as a diprotic acid, with either methyl orange or phenolphthalein as indicators.

H_2P and KHP . For H_2P the ionization constants are well separated ($K_1/K_2 = 200$), but still they are not sufficiently different to allow accurate titration of H_2P as a monoprotic acid. However, H_2P is strong enough to titrate accurately as a diprotic acid, using phenolphthalein as an indicator. KHP may be crystallized with sufficient purity for use as a primary standard, and may be accurately titrated with a strong base. The properties of KHP are given on page 369.

H_3PO_4 . The ionization constants for H_3PO_4 are extremely well separated, since $K_1/K_2 = 1.1 \times 10^5$, and $K_2/K_3 = 1.4 \times 10^5$. H_3PO_4 may therefore be determined either as a monoprotic or as a diprotic acid. However, H_3PO_4 cannot be titrated as a triprotic acid; HPO_4^{2-} is comparable in weakness to water, and there is no appreciable inflection at the third equivalence point. Methyl orange is a suitable indicator for the first equivalence point, and phenolphthalein is suitable for the second. The slopes at both equivalence points are considerably less steep than the slope for the HCl-NaOH titration, and the precision of the H_3PO_4 titration is considerably poorer. Because of the carbonate error (p. 358), the methyl orange end point is more accurate than the phenolphthalein. If an indicator is used, titration conditions should be carefully controlled for high precision, and the titration should be carried to a definite color tint of the indicator. Use of the pH meter to establish the inflection point is preferable to the use of indicators.

The fact that H_3PO_4 may be titrated as either a monoprotic or a diprotic acid permits analysis of phosphate mixtures, as described on page 376.

Na_2CO_3 . The titrimetric behavior of Na_2CO_3 is of great importance for several reasons. (1) Na_2CO_3 is one of the few primary standard bases. (2) Carbonate is an important constituent of limestone, natural waters, and soda ash, and is frequently met in commercial analysis.

(3) The presence of carbonate as an impurity is a source of error in all acid-base titrations.

The ionization constants of H_2CO_3 are sufficiently well separated so that Na_2CO_3 may be titrated as a monoequivalent base, using phenolphthalein, or as a diequivalent base, using methyl orange ($K_1/K_2 = 6000$). HCO_3^- is a very weak acid, and titration of $\text{CO}_3^{=}$ with standard HCl would give a very sharp end point, were $\text{CO}_3^{=}$ only a monoequivalent base. However, the sharpness of the phenolphthalein end point is much reduced by the tendency of HCO_3^- to form H_2CO_3 , which prevents the $p\text{H}$ from dropping rapidly after the first equivalence point is passed. The second equivalence point is also only moderately sharp, since the H_2CO_3 formed is only a moderately weak acid. As in the case of H_3PO_4 , the precision with which these equivalence points may be established is considerably poorer than for a strong acid-strong base titration. Titration to the methyl orange end point is preferred, whenever possible; not only is the curve at the second inflection point steeper, but the carbonate error is more easily avoided.

The fact that Na_2CO_3 may be titrated as either a monoequivalent or a diequivalent base allows analysis of $\text{NaOH-Na}_2\text{CO}_3$ or $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$ mixtures, as described on page 795.

Example 1. What is $[\text{H}_3\text{O}^+]$ when 10.00 ml HCl are added in the titration of Na_2CO_3 under the conditions of Fig. 18.9?

The 10.00 ml of 0.1000 M HCl (or 1.000 mmole) react with the 50.00 ml of 0.1000 M Na_2CO_3 (or 5.000 mmoles), forming 1.000 mmole NaHCO_3 and leaving 5.000 - 1.000, or 4.000 mmoles Na_2CO_3 in a total volume of 50.00 + 10.00, or 60.00 ml. The NaHCO_3 concentration is 1.000/60.00, or 0.01667 M , while the concentration of Na_2CO_3 is 4.000/60.00, or 0.06667 M .

The principal equilibrium is



Letting $[\text{OH}^-] = x$, $[\text{HCO}_3^-] = 0.01667 + x$, and $[\text{CO}_3^{=}] = 0.0667 - x$. Substituting these concentrations into the ionization-constant expression,

$$x, \text{ or } [\text{OH}^-] = 6.38 \times 10^{-4} M$$

$$[\text{H}_3\text{O}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1.00 \times 10^{-14}}{6.38 \times 10^{-4}} = 1.57 \times 10^{-11} M$$

With the calculated value for $[\text{H}_3\text{O}^+]$, the assumption made in setting up the problem may be tested by finding if there are appreciable amounts of carbonate in forms other than $\text{CO}_3^{=}$ and HCO_3^- . Thus

$$[\text{H}_2\text{CO}_3] = \frac{[\text{H}_3\text{O}^+][\text{HCO}_3^-]}{K_1} = \frac{1.58 \times 10^{-11} \times 0.0173}{3.5 \times 10^{-7}} = 7.8 \times 10^{-7}$$

This concentration of H_2CO_3 is negligible compared to the concentrations of $\text{CO}_3^{=}$ and of HCO_3^- , justifying the foregoing assumption.

Example 2. The following "landmarks" are useful in making quick approximations of the shapes of titration curves for diprotic acids for which $K_2 \ll K_1 \ll 1$. Their derivations are left as exercises for the student.

(a) At the beginning of the titration, when the solution contains only H_2A at a concentration C ,

$$[H_3O^+] = \sqrt{K_1 C}$$

(b) Halfway to the first inflection point,

$$[H_3O^+] = K_1$$

(c) At the first inflection point,

$$[H_3O^+] = \sqrt{K_1 K_2}$$

(d) Halfway between the first and second inflection points,

$$[H_3O^+] = K_2$$

(e) At the second inflection point,

$$[H_3O^+] = \sqrt{K_2 K_w / C}$$

18E. EXPERIMENTS

Standard HCl and NaOH solutions are prepared and checked against each other in Exp. 18.1. These two standard solutions are then used for the following determinations: Na_2CO_3 by titration with standard HCl (Exp. 18.2); KHP by titration with standard NaOH (Exp. 18.3); H_3PO_4 (Exp. 18.4) or a mixture of H_3PO_4 and HCl (Exp. 18.5) by titration with standard NaOH, a pH meter being used; NH_3 by the Kjeldahl method (Exp. 18.6). Preparation of unknown samples is discussed in the Supplement (p. 799).

EXPERIMENT 18.1. PREPARATION OF STANDARD HCL AND NaOH SOLUTIONS

Approximately 0.1 *N* solutions are prepared by diluting conc. HCl and saturated NaOH. The HCl solution is standardized against Na_2CO_3 as a primary standard, and the NaOH against KHP. The solutions are then checked by titration against each other, and the best value for the concentration of each is chosen.

PROCEDURE

1. *Preparation and storage of 0.1 N HCl.* (a) Gently boil somewhat more than a liter of distilled water for 5–10 minutes. (Notes 1, 2.) (b) Measure into the small graduate sufficient conc. HCl to prepare 1 l of 0.1 *N* solution. (Note 3.) Transfer the HCl to a 1-l narrow-

necked glass-stoppered bottle containing about 1 l of boiled water. (Note 4.) Mix contents, and label properly. (Note 5.)

2. *Preparation and storage of 0.1 N NaOH.* (a) In the small graduate, measure out sufficient saturated NaOH to prepare a liter of 0.105 N solution. (Note 6.) (b) Transfer immediately to a 1-l rubber-stoppered borosilicate glass bottle containing about 1 l of boiled water. (Notes 4, 7.) Mix contents, and label properly. (Note 5.)

3. *Titration of HCl with NaOH.* (a) Fill one 50-ml buret with the standard HCl, and the other with the NaOH. (Note 8.) (b) Run a 40-ml portion of the HCl into a 250-ml Erlenmeyer flask, add 2 drops of phenolphthalein indicator, and titrate with the NaOH to the faintest tinge of pink that persists for 15 seconds while the contents are being swirled. (Notes 9, 10.) (c) Perform triplicate titrations. (Note 11.) (d) Compute V , the average milliliters of NaOH required per milliliter of HCl. (Notes 12, 13.)

4. *Standardization of HCl with Na_2CO_3 .* (a) Dry 1.2–1.4 g of reagent-grade Na_2CO_3 in a weighing bottle at 150–160°C for 2 hours. Cool and store the loosely stoppered bottle in the desiccator. (Notes 14, 15.) (b) Into a 250-ml beaker weigh precisely 0.9–1.2 g of the dried Na_2CO_3 . Transfer quantitatively to the calibrated 250-ml volumetric flask, dilute to volume, and mix well. (Notes 16–18.) (c) Pipet triplicate 50-ml aliquots of the Na_2CO_3 solution into 250-ml Erlenmeyer flasks, add 3 drops of methyl red–bromocresol green mixed indicator, and titrate with the HCl to a faint pink. Interrupt the titration, heat the solution to a gentle boil for 2 minutes to expel CO_2 , and cool the flask contents below 30°C under the water tap. If the end point has not been overrun, the indicator will reassume its green color. Complete the titration with HCl to a sharp color change. Calculate the average normality of the HCl solution, calling it N_{acid} . (Notes 19–21.)

5. *Standardization of NaOH with KHP.* (a) Into 250-ml Erlenmeyer flasks weigh precisely triplicate 0.7–0.9-g portions of reagent-grade KHP that has been dried at 100°C for 2 hours. (Notes 22, 23.) (b) Add about 50 ml of boiled water and 2 drops of phenolphthalein, and titrate to the faintest tinge of pink that persists for 15 seconds after swirling. (Notes 9, 24.) (c) Calculate the average base normality, calling this N_{base} . (Note 25.)

6. *Calculations.* (a) See page 367 for a typical summary data page. (b) Choose the best values for the standard acid and base normalities, and record these on the labels of the reagent bottles. (Note 26.)

NOTES

(1) The boiling is best done in the 1-l Florence flask. To prevent bumping the flask should not be filled above 800 ml. The use of two or three small boiling chips

SUMMARY DATA PAGE

EXP. 18.1. PREPARATION OF STANDARD HCl AND NaOH

Date begun.....

John Brown

Date completed.....

Locker No.....

Titration of HCl with NaOH* (Data and calcs., p.)

Determination	1	2	3
Ml HCl			
Ml NaOH			
Ml NaOH/ml HCl			
Av. ml NaOH/ml HCl, V .			

Direct standardization of HCl* (Data and calcs., p.)

Grams Na_2CO_3	
Ml of solution in which Na_2CO_3 is dissolved	
Aliquot of Na_2CO_3 solution titrated	
Ml of HCl used in titration.	First
	Second
	Third
	Average
Av. HCl normality, $\frac{N_{\text{acid}}}{VN_{\text{base}}}$	
Best HCl normality	

Standardization of NaOH* (Data and calcs., p.)

Determination	1	2	3
Grams KHP			
Ml NaOH			
NaOH normality			
Av. NaOH normality, $\frac{N_{\text{base}}}{N_{\text{acid}}/V}$			
Best NaOH normality			

* All volumes corrected for temperature and blanks, if necessary.

will also help to prevent bumping. After boiling is complete, cover the flask closely with a watch glass, and allow the contents to cool sufficiently so that they may be poured into a 1-l narrow-necked bottle for storage. The storage bottle should always be kept stoppered, except when the solution is being withdrawn. Three 800-ml batches suffice for both standard solutions and for blank determinations. Never stopper the Florence flask tightly immediately after boiling, or a vacuum may develop and the thin, flat-bottomed flask may implode on cooling.

(2) The concentration of CO_2 in equilibrium with normal amounts of CO_2 in air is only $1.4 \times 10^{-5} M$, which is inappreciable when 0.1 *N* solutions are used. The water is boiled only to remove abnormally large amounts of CO_2 that may be present.

(3) From Appendix IV, conc. HCl is 12.4 *M*. Hence the volume of conc. HCl required is $1000 (0.10/12.4) = 8.1 \text{ ml}$.

(4) The transfer need not be quantitative, and may be made with a small funnel. Care should be exercised to avoid contaminating the neck of the bottle with the concentrated solution.

(5) Mixing must be thorough. Invert the stoppered bottle several times during mixing. Also, remove and replace the stopper occasionally during mixing, to ensure that no concentrated solution adheres between stopper and neck. After preparation of the solution, always keep the bottle stoppered, except when withdrawing solution.

(6) Reagent-grade NaOH may contain considerable Na_2CO_3 , but fairly complete removal of Na_2CO_3 may be achieved, owing to its low solubility in saturated NaOH. Properly prepared, saturated NaOH contains only a few millimoles of Na_2CO_3 per mole of NaOH. Saturated NaOH is best prepared in large batches and dispensed from the stock room (Appendix IV). Small batches may be prepared with ordinary student equipment, a filter crucible being used to remove Na_2CO_3 , but these batches contain more Na_2CO_3 than large batches.

The base is made slightly more concentrated than the acid for convenience in Exps. 18.4 and 18.5, where 50-ml aliquots of the acid will be titrated with the base. If the acid is more concentrated, more than one buretful of base will be required.

(7) Basic solutions should not be stored in glass-stoppered bottles, for the stoppers become frozen. Base solutions should not be stored in plastic bottles, which are permeable to CO_2 and other gases (T1).

(8) After withdrawing portions of standard solution, wipe off droplets adhering to the lip of the bottle with a clean tissue. Replace the stopper immediately after pouring.

(9) The color soon fades as the solution absorbs CO_2 from the air.

(10) If the required volume of base is outside the range of 35–40 ml, dilute the more concentrated solution with an appropriate amount of boiled water, and mix well. Flush and refill the buret, and repeat the titration.

(11) The relative range of triplicates is less than 0.1% for excellent work.

(12) To avoid confusion in reporting and discussing results, the same symbolism should be used by all members of the class.

(13) It must be understood that the calculated value of *V* applies only when phenolphthalein is used as an indicator. If the base contains carbonate, and if titration is made to any other end-point *pH*, *V* differs slightly from the phenolphthalein value.

(14) Na_2CO_3 is among the best primary standards for HCl solutions (see page 363). Other primary standards are described in the Supplement (p. 793).

(15) Na_2CO_3 absorbs water to form a fairly stable hydrate, and CO_2 , to form NaHCO_3 . Temperatures considerably in excess of 100°C are necessary to drive off water and CO_2 (C1).

(16) Show that a 50-ml aliquot of this solution requires about 35–45 ml of 0.1 *N* HCl for titration.

(17) Theoretically, it is not necessary to use boiled water, since CO₂ is formed at the equivalence point.

(18) The Na₂CO₃ solution is basic, and should be prepared and used on the same day. If it must be stored, Na₂CO₃ solution must never be left in the volumetric flask, which may become etched, or whose stopper may become frozen.

(19) The relative range of triplicate titrations is less than 0.2% for excellent work.

(20) The HCl normality is

$$\frac{\text{mg Na}_2\text{CO}_3 \text{ in aliquot}}{105.99/2} \times \frac{1}{\text{ml HCl used}}$$

(21) Figure 18.10 is a calculated titration curve. Although the calculated equivalence-point pH of 4.05 is probably not correct (since activity effects and the escape of CO₂ are neglected), the curve does show that the end point is not sharp.

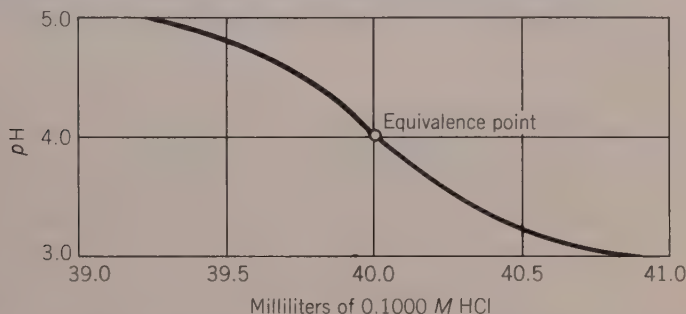
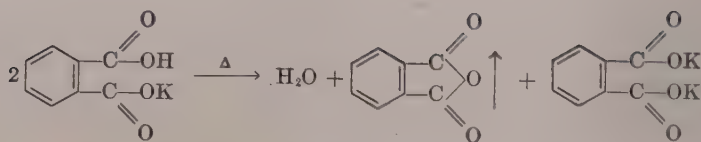


FIG. 18.10. Titration of Na₂CO₃ with HCl—Conditions: 50.00 ml of 0.0400 *M* Na₂CO₃ titrated with 0.1000 *M* HCl. *K*₁ for H₂CO₃ is 3.5×10^{-7} . Activity effects disregarded. All CO₂ retained in solution.

Since it is the presence of CO₂ that causes the poor end point, greater accuracy is achieved by driving off the CO₂ before establishing the end point. In going to the first pink color of the mixed indicator (pH 4.5), almost all of the carbonate is converted to H₂CO₃, which is quantitatively removed by boiling. Removal of CO₂ causes an increase in pH, and the indicator color becomes green again after boiling. After boiling, NaCl is the principal solute, and titration of the small amount of remaining base gives an end point almost as sharp as that for a strong acid–strong base titration. The end point for the mixed indicator is marked by the gray between the green basic color and the pink acid color (see Supplement, p. 782).

(22) Show that this sample range requires about 35–45 ml of 0.1 *N* base for titration.

(23) KHP is one of the best primary standards for NaOH solutions. A titration curve is shown in Fig. 18.9 (p. 362). Other primary standards are described in the Supplement (p. 793). The KHP end point is sharp and choice of an indicator is uncritical; phenolphthalein is satisfactory. The high equivalent weight is an advantage, for the large samples required make ordinary weighing errors negligible. Solid KHP is stable and nonhygroscopic, and may be safely dried to constant weight at 100°C. Temperatures over 125°C, however, cause conversion to phthalic anhydride, which sublimes, leaving K₂P as an impurity.



(24) The blank correction is negligible. This may be verified by titration of a 50-ml portion of the boiled water used to dissolve the KHP. Less than 0.02 ml of 0.1 *N* base should be required.

(25) For excellent work, the relative range of triplicate determinations of the normality should be less than 0.2%.

(26) From the data of this experiment, two estimates of the acid normality are obtained: N_{acid} and VN_{base} . For excellent work, these two estimates should differ by less than 0.1%. If agreement between the two estimates is good, the best value for the standard acid normality is the mean of the two estimates. If agreement is poor, the discrepancy should be resolved before unknown samples are analyzed (see Note 14, p. 293). In similar fashion, the two estimates of the base normality are N_{base} and N_{acid}/V .

EXPERIMENT 18.2. DETERMINATION OF Na_2CO_3

A sample containing only Na_2CO_3 and NaCl is analyzed by titration with standard HCl , according to the method of Exp. 18.1.

PROCEDURE

1. Dry sample at 150–160°C for 2 hours. (Note 15, p. 368.)
2. Into a 250-ml beaker weigh precisely 1.0–1.2 g of sample, transfer to the 250-ml volumetric flask, dissolve, make up to volume, and mix well. (Note 1. Also Note 17, p. 369.)
3. Pipet triplicate 50-ml aliquots of the sample solution into 250-ml Erlenmeyer flasks, and titrate according to the procedure of step 4 on page 366. (Notes 2, 3.)
4. Calculate the average milliliters of HCl required per 50-ml aliquot of sample solution, and then calculate the % Na_2CO_3 in the sample. (Note 4.)

NOTES

- (1) If the sample contains 80–100% Na_2CO_3 , and if 30–45 ml of 0.100 *N* acid are to be used in titration, the lower limit of sample size is

$$\begin{array}{c} \text{meq Na}_2\text{CO}_3 \text{ required} \\ \text{in 50-ml aliquot} \end{array} \left[0.100 \times 30 \right] \times \frac{105.99}{2} \times \frac{100}{80} \times \frac{250}{50} \times \frac{1}{1000} = 0.99 \text{ g}$$

mg 80% sample
mg pure Na_2CO_3

In similar fashion, the upper limit of sample size may be computed as 1.19 g. If samples of different composition are used, the instructor will announce the proper sample size.

(2) The relative range of triplicate determinations is less than 0.2% for excellent work.

(3) The blank is negligible and need not be determined.

(4) The % Na_2CO_3 is

$$\frac{(\text{ml HCl}) \times (\text{HCl normality})}{\text{meq HCl} = \text{meq Na}_2\text{CO}_3} \times \frac{105.99}{2} \times \frac{100}{\left(\frac{\text{mg sample}}{\text{in aliquot}} \right)} = \text{mg Na}_2\text{CO}_3$$

EXPERIMENT 18.3. DETERMINATION OF KHP

A sample containing only KHP and K_2SO_4 is analyzed by titration with standard NaOH, according to the procedure of Exp. 18.1.

PROCEDURE

1. Into 250-ml Erlenmeyer flasks weigh precisely triplicate 0.8–0.9-g portions of the sample, which has been dried for 2 hours at 100°C . (Note 1. Also Note 23, p. 369.)

2. To each sample add 50 ml of boiled water and 2 drops of phenolphthalein. Titrate immediately with standard base. (Notes 2, 3.)

3. Calculate the average % KHP in the sample. (Note 4.)

NOTES

(1) Show that this range of weights of 80–100% KHP samples requires about 30–45 ml of 0.1 *N* base. If samples of different composition are used, the instructor will announce the proper sample size.

(2) Complete the titration as quickly as possible, since CO_2 may be absorbed from the air.

(3) The blank is negligible and need not be determined.

(4) The range of triplicate determinations should be less than 0.2% for excellent work.

EXPERIMENT 18.4. TITRATION OF H_3PO_4 WITH A pH METER

A solution of H_3PO_4 is titrated as a monoprotic acid with standard NaOH. The titration curve is determined with a pH meter, and the inflection point is selected as the equivalence point. Error due to carbonate in the standard base is observed and reduced to a minimum.

PROCEDURE

1. *Withdrawal of unknown. Equipment.* Each student is scheduled in advance to use the pH meter, and he must plan to carry out the ti-

trations during his allotted time. The calibrated 250-ml volumetric flask should be labeled with the student's name, locker number, and the experiment number, and deposited with the instructor during the laboratory period preceding the one scheduled for use of the meter. The unknown sample may then be withdrawn at the beginning of the scheduled period.

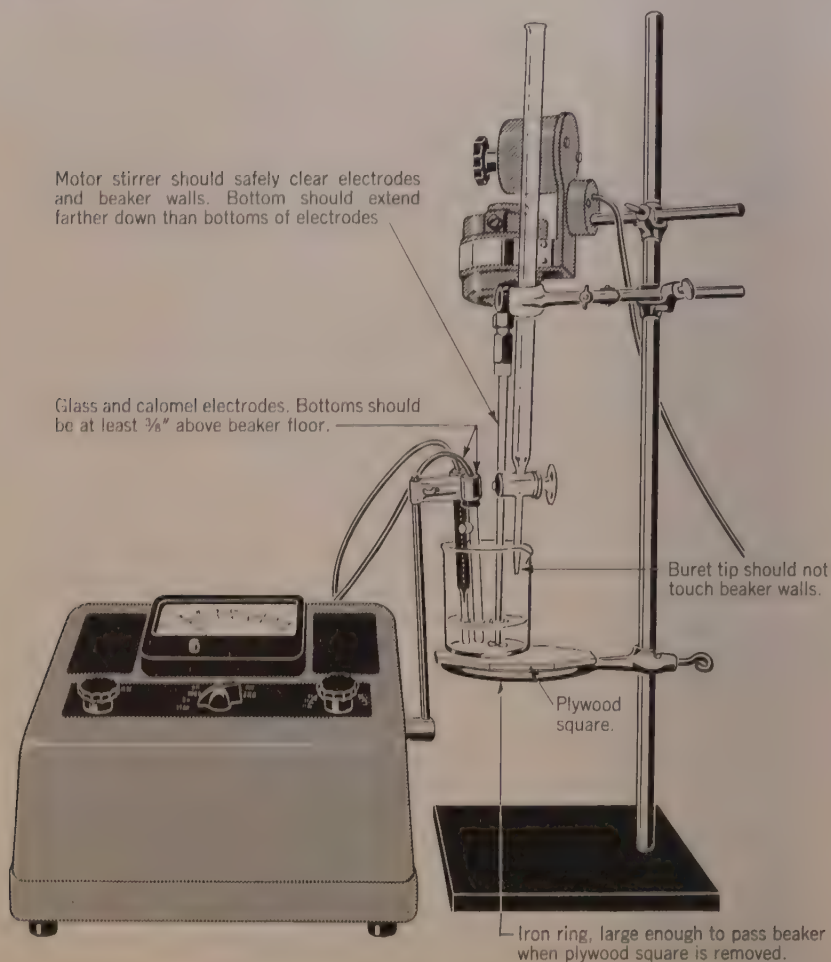


FIG. 18.11. Equipment for Performing a pH Titration

Equipment for carrying out a pH titration is shown in Fig. 18.11. The beaker rests on a plywood square, which in turn rests upon an iron ring having a diameter greater than that of the beaker. To remove the

beaker without disturbing the rest of the assembly, lift the beaker slightly, slide the plywood square away, and lower the beaker through the iron ring. Replacement of the beaker is accomplished similarly. The height of the ring is adjusted so that the bottom of the stirrer barely clears the bottom of the beaker. The electrodes are mounted so that their ends are one-fourth to one-half inch above the bottom of the stirrer; thus the electrodes cannot be hit when the beaker is raised or lowered. The student's buret is mounted in the clamps provided, so that reading and manipulation are convenient.

2. *Operation of the pH meter.* (Note 1.) The pH meter and associated equipment should not be used until detailed directions have been obtained from the instructor. After the experiment has been completed, the pH meter and its associated equipment should be left in perfect condition for the next user. Any breakage or malfunction should be reported immediately to the instructor.

3. *Restandardization of the standard base.* (Note 2.) (a) Prepare equipment for titration. Clean the electrodes with a stream of water from the wash bottle. Rinse the buret and fill to the zero mark with the base to be restandardized. Put an empty, clean (not necessarily dry), 250-ml beaker into position for the titration. (b) Into the beaker pipet a 50-ml aliquot of standard HCl. Run base rapidly into the beaker, to within about 2 ml of the equivalence point. (Note 3.) Carefully turn on the stirrer to give a low rate of stirring throughout the rest of the titration. (Note 4.) Touch off the buret tip with a stirring rod especially reserved for this purpose, and immerse the end of the rod into the titrated solution. (Note 5.) Read the volume and pH, and plot this pair of readings as the first point of the titration curve. (Notes 6, 7.) (c) Add 0.5 ml of base, touch off the tip, read the volume and pH, and plot the second point on the titration curve. Continue adding base and plotting points until the curve begins to level off around pH 10. (Note 8.) (d) Draw the best smoothed curve through the experimental points. Select the end-point volume of base. (Notes 9, 10.) (e) Perform a duplicate titration, and calculate the average volume of base required per 50-ml aliquot of standard HCl. (Note 11.) Calculate the "pH 4-5 normality" of the base, using the standard acid normality of Exp. 18.1. (Note 12.)

4. *Titration of the H_3PO_4 sample.* (Note 13.) (a) Dilute the H_3PO_4 sample to volume in the 250-ml flask, using boiled water, and mix well. (Notes 14, 15.) (b) Pipet a 50-ml aliquot of the H_3PO_4 solution into the titration beaker, and titrate with standard base, using the techniques of steps 3b and 3c above. (Notes 16, 17.) (c) Draw the smoothed titration curve, and select the inflection point as the end point. (d) Perform a duplicate titration, and calculate the average volume of base

required per 50-ml aliquot of H_3PO_4 solution. (Note 18.) (e) Calculate the grams of P_2O_5 in the whole sample issued. (Note 19.)

NOTES

(1) The $p\text{H}$ meter is an instrument that is calibrated to give directly the $p\text{H}$ (really $p\text{a}_{\text{H}}$, see footnote, p. 318) of the solution in which the electrodes are immersed. A voltage is generated between the electrodes that is a function of the $p\text{H}$ of the solution, and that may be taken as a measure of the $p\text{H}$. This voltage is of the order of tenths of a volt, but cannot be measured with a simple voltmeter because the resistance of the glass electrode is very high. The $p\text{H}$ meter is simply a potentiometer for measuring voltage across a very high resistance. It is not possible to present adequately the theory of $p\text{H}$ measurement until after the fundamentals of redox theory are presented. The purpose of this experiment, therefore, is not to describe the theory of the $p\text{H}$ meter, but simply to show how it is used in a titration.

(2) The NaOH used in Exps. 18.1 to 18.3 is standardized to a phenolphthalein end point ($p\text{H}$ 8–9). Since Na_2CO_3 may be present in the standard base, and since it must be used to the $p\text{H}$ 4–5 end point in this experiment, restandardization of the base is necessary. Restandardization is made against the standard HCl of Exp. 18.1.

(3) The volume of base required may be calculated approximately from its phenolphthalein normality of Exp. 18.1. Add 3 ml less than this.

(4) A heavy hand or too high a stirring rate may cause the beaker contents to be thrown out. The stirrer blades must safely clear the electrodes and beaker walls.

(5) The buret tip must be touched off after each increment of base is added, so that the volume of base added to the solution corresponds exactly to the buret reading. If this is not done, the experimental points of the titration curve are scattered.

(6) The $p\text{H}$ may drift for a few seconds after addition of a portion of base, until the solution becomes homogeneous. The $p\text{H}$ should be read after it reaches a steady state.

(7) A blank sheet of graph paper should be prepared before the titration is begun, so that $p\text{H}$ meter and buret readings may be plotted directly as the titration proceeds, instead of these data being tabulated and plotted afterwards. This procedure is advantageous not only because it saves time, but also because the progress of the titration may be more easily perceived, and because the result is immediately available. An appropriate scale is about 0.5 $p\text{H}$ unit per cm (ordinates) and 0.5 ml per cm (abscissae).

(8) In the region of the equivalence point, adjust the size of the portions of standard base added to give a change of 0.1–0.2 $p\text{H}$ unit per portion, but add no portions smaller than 1 drop.

(9) The end point is not selected at the inflection point but is chosen as the volume of base required to reach a $p\text{H}$ identical with the end-point $p\text{H}$ in the H_3PO_4 titration of step 4. This is essentially a titer method of standardizing the base for H_3PO_4 determination, in which error due to carbonate in the standard base is avoided by the base's being standardized to the same $p\text{H}$ as that at the end point in the titration of the unknown H_3PO_4 sample. Thus, if the inflection point in the H_3PO_4 titration of step 4 comes at $p\text{H}$ 4.63, then $p\text{H}$ 4.63 is the end point to which the base should be standardized, regardless of where the inflection point comes in the HCl - NaOH titration curve.

(10) Data for the restandardization curve should be carefully taken and preserved for further use in Exp. 18.5.

(11) Duplicate titrations should agree within 0.04 ml for excellent work.

(12) For reasons given in Note 9, the calculated base normality is appropriate only for titration of H_3PO_4 to the first equivalence point (pH 4–5), and is therefore called the “ pH 4–5 normality.” It is calculated as

$$\frac{(N_{\text{acid}})(\text{ml of acid in aliquot titrated})}{\left(\begin{array}{l} \text{ml of base required for titration to a } \text{pH} \text{ identical with} \\ \text{the first end-point } \text{pH} \text{ in titrating the } \text{H}_3\text{PO}_4 \text{ sample} \end{array} \right)}$$

(13) It was shown on page 359 that the titration of H_3PO_4 as a monoprotic acid is more accurate than its titration as a diprotic acid. An enlarged curve for the titration to NaH_2PO_4 is shown in Fig. 18.12, calculated for conditions approximating those of this experiment. Although the calculated inflection-point pH of 4.7 is probably not correct, since activity effects are neglected, the curve does show that the end point is not sharp. The pH meter is more accurate and precise for such a titration than chemical indicators.

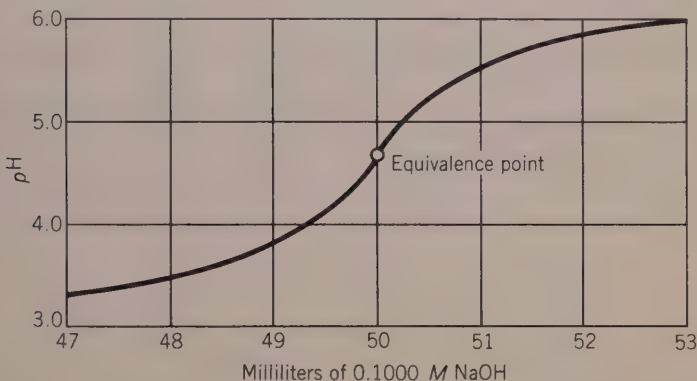


FIG. 18.12. Titration of H_3PO_4 with NaOH —Conditions: 50.00 ml of 0.1000 M H_3PO_4 titrated with 0.1000 M NaOH . K_1 and K_2 for H_3PO_4 are 0.0071 and 6.2×10^{-8} , respectively. Activity effects disregarded. Volumes assumed additive.

(14) The issued sample contains such an amount of H_3PO_4 that a 50-ml aliquot of the diluted solution requires 30–45 ml of 0.1 N base for titration to the NaH_2PO_4 end point (pH 4–5). If samples of different composition are used, the instructor will announce the proper sample size.

(15) In this determination, calculations are based on the pH 4–5 end point. Here the small amount of CO_2 introduced with unboiled water would cause a slight but inappreciable error, and unboiled water could be used. However, in titration to the pH 9–10 end point, the CO_2 introduced with unboiled water causes an appreciable error. Boiled water is recommended in order that calculations based on the pH 9–10 end point may be made if desired.

(16) With an unknown sample, there is no way of calculating where the end point will fall. However, with the stirrer turned on, base may be added rapidly and with-

out recording volumes, up to around pH 3.5 (Fig. 18.12). From here, base should be added in definite increments, as described in step 3c.

(17) The titration may be continued to the Na_2HPO_4 end point (pH 9–10), to verify its inferiority. It should also be noted that the volume of base required to reach the second end point is considerably more than twice the volume required to reach the first end point, if the base contains carbonate. A mode of correcting for the carbonate error is given in Exp. 18.5.

(18) For excellent work, duplicates should agree within 0.04 ml.

(19) The grams of P_2O_5 in the whole sample are

$$\left(\begin{array}{c} \text{pH 4-5} \\ \text{normality of base} \end{array} \right) \times \text{ml base} \left| \begin{array}{c} \times \frac{141.94}{2} \\ \text{meq of base} \end{array} \right| \times \frac{250}{50} \left| \begin{array}{c} \times \frac{1}{1000} \\ \text{mg P}_2\text{O}_5 \text{ in} \\ \text{whole sample} \end{array} \right|$$

mg P_2O_5 in 50-ml aliquot

Since $1\text{P}_2\text{O}_5 = 2\text{H}_3\text{PO}_4 = 2$ equivalents, the equivalent weight of P_2O_5 is one-half its molecular weight.

EXPERIMENT 18.5. TITRATION OF AN HCl - H_3PO_4 MIXTURE

An aqueous solution containing only HCl and H_3PO_4 is analyzed by titration with standard NaOH . The titration curve is determined with a pH meter, and the HCl and H_3PO_4 contents are calculated from the two inflection points. Because of the complex nature of this experiment, it is desirable to perform the simpler Exp. 18.4 first.

THEORY

Because H_3PO_4 may be titrated either as a monoprotic or as a diprotic acid, a mixture of H_3PO_4 and a strong acid like HCl may be titrated to two end points to give both the H_3PO_4 and the HCl contents, as in the following example.

Example. A 50.00-ml portion of a solution containing HCl and H_3PO_4 requires 27.95 ml of 0.1000 *N* carbonate-free base for titration to the methyl orange end point. Another 50.00-ml portion requires 49.63 ml of the standard base to the phenolphthalein end point. Assuming that end-point errors are negligible, find the H_3PO_4 and HCl concentrations in the original solution.

To the methyl orange end point:



$$\left(\begin{array}{c} \text{mmoles HCl} \\ + \text{mmoles} \\ \text{H}_3\text{PO}_4 \end{array} \right) = \left(\begin{array}{c} \text{meq base} \\ \text{used to methyl} \\ \text{orange end point} \end{array} \right)$$

$$= 0.1000 \times 27.95 = 2.795 \quad (a)$$

To the phenolphthalein end point:



$$\left(\begin{array}{c} \text{mmoles HCl} \\ + 2 \times \text{mmoles} \\ \text{H}_3\text{PO}_4 \end{array} \right) = \left(\begin{array}{c} \text{meq base used} \\ \text{to phenolphthalein} \\ \text{end point} \end{array} \right)$$

$$= 0.1000 \times 49.63 = 4.963 \quad (b)$$

From the difference between Eqs. *a* and *b*, the number of mmoles H_3PO_4 in the 50-ml aliquot is $4.963 - 2.795$, or 2.168 . The H_3PO_4 molarity is therefore $2.168/50.00$, or $0.04336 M$.

By difference, the number of moles HCl in the 50-ml aliquot is $2.795 - 2.168$, or 0.627 . The HCl molarity is therefore $0.627/50.00$, or $0.01254 M$.

Actually, it is unnecessary to use two aliquots for titration. Both methyl orange and phenolphthalein may be added to a single aliquot, which may then be titrated with standard base, first to the methyl orange end point, and then further to the phenolphthalein end point. Neither indicator interferes with the other. In practice, the pH meter gives higher accuracy than indicators.

The principle of this method of analysis is extendable to any mixture of phosphates, and/or HCl, and/or NaOH (see Supplement, p. 797).

PROCEDURE

1. *Withdrawal of unknown.* See step 1, page 372.
2. *Operation of pH meter.* See step 2, page 373.
3. *Restandardization of base.* (Note 1.)
4. *Titration of the HCl-H₃PO₄ sample.* (a) Dilute the sample to volume in the 250-ml volumetric flask, using boiled water, and mix well. (Notes 2, 3.) (b) Titrate a 50-ml aliquot of the diluted sample solution to the first inflection point (pH 4–5), proceeding just far enough past this point to establish it with certainty. Record accurately the total volume of base added. (c) Refill the buret to the zero mark, and continue the titration to the second inflection point (pH 9–10), titrating only far enough past this point to establish it with certainty. (d) Perform the titration in duplicate. (Note 4.)
5. *Calculations.* (a) Compute the average volumes of base required to the first (pH 4–5) and to the second (pH 9–10) inflection points. From these volumes and the appropriate base normalities, calculate the milliequivalents of base used to the first and second end points. (b) From the milliequivalents of base used to the first end point, calculate and report the total millimoles of HCl plus millimoles of H_3PO_4 in the whole issued sample. (c) Calculate and report the millimoles of H_3PO_4 in the whole issued sample. (Note 5.)

NOTES

(1) In this experiment, the standard base is used to titrate the $\text{HCl-H}_3\text{PO}_4$ sample to two end points— pH 4–5, at which HCl is converted to NaCl , and H_3PO_4 to NaH_2PO_4 ; and pH 9–10, at which HCl is converted to NaCl , and H_3PO_4 to Na_2HPO_4 . Since Na_2CO_3 is present in the base, the base normality depends upon the end-point pH , and two base normalities must be used, a pH 4–5 normality, and a pH 9–10 normality. The restandardization titration curve of Exp. 18.4 may be used, or, if this experiment was not performed, the base may be restandardized as in step 3, page 373. The pH 4–5 normality is

$$\frac{(N_{\text{acid}})(\text{ml of acid in aliquot titrated})}{\left(\begin{array}{l} \text{ml of base required for titration to a } \text{pH} \text{ identical with} \\ \text{the first end-point } \text{pH} \text{ in titrating the } \text{HCl-H}_3\text{PO}_4 \text{ sample} \end{array} \right)}$$

This pH 4–5 normality should be close to that of Exp. 18.4, but not necessarily identical, since the end-point pH in the titration of the $\text{HCl-H}_3\text{PO}_4$ sample of this experiment is not necessarily identical with the end-point pH for the titration of the H_3PO_4 sample of Exp. 18.4. The pH 9–10 normality is calculated similarly.

(2) The issued sample contains such an amount of HCl plus H_3PO_4 that titration of a 50-ml aliquot of the diluted solution requires 35–45 ml of 0.1 N base for titration to the first end point. Completion of the titration to the second end point may require any volume of standard base up to the volume required to reach the first end point. If samples of different composition are used; the instructor will announce the proper sample size.

(3) The titer method is used in this experiment, and error due to carbonate in the standard base is avoided by standardizing the base to the same end-point pH as in titrating the $\text{HCl-H}_3\text{PO}_4$ sample. This method does not compensate for CO_2 introduced with reagents; hence to avoid troublesome determination of blank corrections, boiled water is used to dissolve the sample.

(4) For excellent work, duplicates should agree within 0.04 ml for the first end point, and within 0.08 ml for the second end point.

(5) These values are requested because they are most convenient for the instructor to grade. The HCl and H_3PO_4 contents could be reported in any other terms desired. It is instructive to calculate the grams of HCl and grams of H_3PO_4 in the sample issued, but these values need not be reported unless they are requested by the instructor.

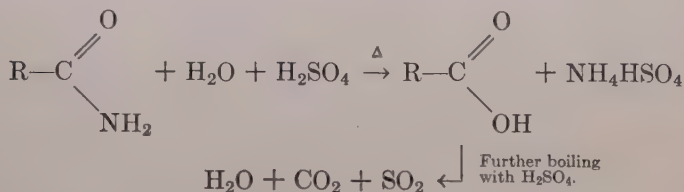
EXPERIMENT 18.6. KJELDAHL DETERMINATION OF N AS NH_3

THEORY

Nitrogen is an important element in biological substances, such as proteins, peptides, and certain vitamins. It also occurs in certain classes of simple organic compounds, such as amines, amides, and nitro compounds. The Kjeldahl method, named after its originator, is most frequently used to determine N in foodstuffs and in fertilizers. In outline, the Kjeldahl method consists of three steps. (1) The organic N is converted to an ammonium salt by digestion with conc. H_2SO_4 .

(2) The ammonium salt is decomposed in basic solution to NH_3 , which is distilled and recovered quantitatively. (3) The NH_3 in the distillate is determined by titration with standard acid.

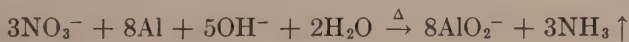
Digestion. In amides and amines N may be converted to ammonium salts by being boiled with conc. H_2SO_4 .



Protein N is of this type, and may also be converted to NH_4HSO_4 in this way.

The digestion is a slow hydrolysis, followed by oxidation of organic matter. Several techniques are used to hasten the reaction. (1) In the Gunning modification, K_2SO_4 is added to the reaction mixture to raise the boiling point of the H_2SO_4 , increasing the rate of reaction. (2) Compounds of Cu, Hg, or Se catalyze the hydrolysis. CuSO_4 is frequently used. (3) Oxidizing agents may be used to aid the decomposition of resistant organic materials. This technique is not so widely used because of the danger of oxidation and loss of N. Kirk gives a critical description of sources of error in the Kjeldahl procedure, especially on the microscale (K6). Swift gives detailed practical instructions for performing the digestion and distillation (S36). Recent developments and improvements are reviewed periodically (B24).

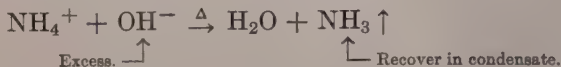
Nitrogen in other kinds of compounds that do not hydrolyze directly to NH_4HSO_4 may sometimes be reduced and then hydrolyzed. Azo, azoxy, and nitro compounds may be treated in this way (D5). In one method, addition of salicylic acid and $\text{Na}_2\text{S}_2\text{O}_3$ to the sample in conc. H_2SO_4 accomplishes this reduction before digestion (F7). Inorganic nitrates may also be determined in this way by Devarda's method, in which nitrate in strongly alkaline solution is reduced directly to NH_3 by Devarda's alloy (45% Al, 5% Zn, 50% Cu). The NH_3 is distilled directly from the alkaline mixture as it is formed.



A recent study of Devarda's method (E3) has revealed a tendency toward loss of N oxides formed by decomposition of intermediate HNO_2 , and yields are poor. Addition of ferrous salts reduces such losses by

complexing and holding intermediate NO until it can be reduced completely.

Distillation and titration. After all N is converted to NH_4HSO_4 , it may be determined in several ways. In most methods the reaction mixture is made basic with excess NaOH, and the NH_3 is removed from all interferences by distillation.

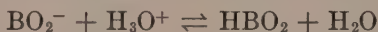


Some NH_3 would be lost if simple condensation of the distillate were attempted, for the pressure of NH_3 from its aqueous solution is appreciable. To prevent loss of NH_3 , the distillate is caught in an acidic solution. In the original Kjeldahl method, the distillate is caught in a measured excess of standard H_2SO_4 , and the excess H_2SO_4 is determined by back titration with standard base. Since the solution at the equivalence point contains $(\text{NH}_4)_2\text{SO}_4$ (pK_a for NH_4^+ is 9.26), methyl red is used as an indicator. The equivalents of NH_3 in the sample are equal to the total equivalents of H_2SO_4 added minus the equivalents of base used in back titration. This method has two disadvantages—the amount of NH_3 is obtained as a difference, and two standard solutions are required.

In the Winkler modification, the NH_3 is caught in an unmeasured excess of boric acid.



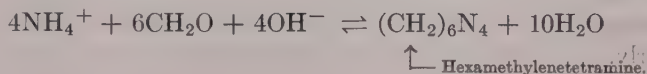
The borate formed is a moderately strong base (pK_b is 4.81), and may be determined by titration with standard HCl, one mole of HCl being required for each mole of NH_3 .



The solution at the equivalence point contains HBO_2 (pK_a is 9.19) and NH_4Cl (pK_a for NH_4^+ is 9.26), so that an indicator transiting in the acid region (pH 5–6) is necessary. Bromocresol green (transition range 3.8–5.4) is satisfactory.

The Marcali-Rieman method eliminates the time-consuming and exacting distillation (R10). In outline, the steps are: (1) After digestion, excess H_2SO_4 is neutralized to the methyl red end point with 10 *N* NaOH. Much carbonate may be introduced with the large volume of NaOH used, and this carbonate must be removed by adding a small excess of 0.1 *N* HCl and boiling. After cooling, the excess HCl is neutralized with 0.1 *N* carbonate-free base just to the methyl red end point (pH 5–6). Up to this point, the amounts of acid and base added need

not be measured. (2) An excess of formaldehyde is added, which brings about the reaction



This reaction is not complete at pH 5-6, but does go to completion as the mixture is titrated with standard base to the phenolphthalein end point. In passing from the methyl red to the phenolphthalein end point, one mole of base is required for each mole of NH_3 in the digestion mixture. Precautions are necessary to eliminate error due to digestion catalysts, formic acid in the reagent formaldehyde, and a rather diffuse phenolphthalein end point.

Micro-Kjeldahl analysis. The Kjeldahl analysis may be performed on the semi-micro- and micro-scales, with modified equipment and techniques. Amounts of N as low as $0.005 \mu\text{g}$ may be detected, and reasonable accuracy may be obtained on samples containing as little as $0.1 \mu\text{g}$ of N. If sample sizes of $0.001 \mu\text{g}$ could be handled, it would be possible to determine the N content of single living cells (K6).

The Dumas method. In the digestion of some compounds, N is not quantitatively converted to NH_3 by the ordinary Kjeldahl procedure, but may be volatilized and lost as nitrogen gas or its oxides, giving low results. The Dumas method is suitable for determining N in any type of compound. The sample is mixed with powdered CuO and heated in a stream of CO_2 . Nitrogen in the sample is converted to nitrogen gas, whereas C and H are converted to CO_2 and water. The nitrogen is collected and measured in a gas buret over 50% KOH , which absorbs and removes CO_2 and water.

PROCEDURE

A sample containing only $(\text{NH}_4)_2\text{SO}_4$ and K_2SO_4 is distilled from alkaline solution, and the NH_3 is collected in 4% boric acid. The NH_3 is titrated in the boric acid solution with standard HCl to the bromocresol green end point, according to the Winkler procedure.

The following instructions do not include digestion. If organic samples requiring digestion must be analyzed, additional instructions must be obtained from the instructor. Distillation equipment is assembled from ordinary student apparatus available from the stock room. Procedures with special or unitized equipment for digestion and distillation are not described.

1. *Preparation of sample.* (a) Into a small beaker weigh 1.2-1.5 g of sample that has been dried for 2 hours at $100-110^\circ\text{C}$. (Note 1.) (b)

Transfer the sample quantitatively to the 250-ml volumetric flask, dissolve, make up to volume, and mix well. (Note 2.)

2. *Preparation of distillation apparatus.* Figure 18.13 shows the distillation apparatus. (Note 3.) Before use, check the following items particularly. (a) All connections and stoppers should be tight, to prevent loss of NH_3 . (b) The flasks should be easily removable. This is best

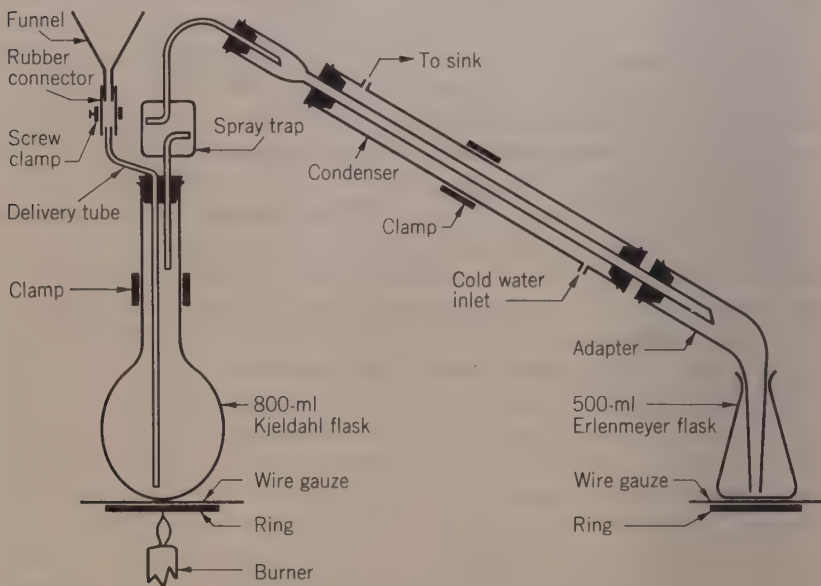


FIG. 18.13. The Kjeldahl Distillation

done by swinging away the rings and lowering the flasks. (c) The burner should give a good flame and be easily adjustable. (d) There should be no leaks in the condenser or its connections. The cooling water should flow only fast enough so that the sink stream is not noticeably warm. The adapter should never become warm. (e) The analysis should be performed as far as possible from sources of NH_3 contamination. NH_3 reagent bottles should not be kept nearby, and NH_3 should not be poured into nearby sinks. (f) Do not begin a distillation unless there is time enough to finish it.

3. *Steaming out apparatus.* Put 250 ml of water, 5 ml of 6 M NaOH, and 2 or 3 boiling chips in the Kjeldahl flask. Let the water drain from the jacket of the condenser, and distill at a brisk boil until the adapter becomes hot and steam issues from it. Continue steaming for 10 minutes. (Note 4.)

4. *Determination of the sample.* (a) Remove the Kjeldahl and re-

ceiving flasks, and rinse them with distilled water. (b) Into the Kjeldahl flask put a 50-ml aliquot of the sample solution, 150 ml of the same batch of water used to dissolve the sample, 2 drops of conc. H_2SO_4 , and 2–3 boiling chips. (Note 5.) Reconnect the Kjeldahl flask. Turn on the cooling water, and bring the contents of the Kjeldahl flask to a brisk boil. Immerse the end of the adapter to a depth of about a quarter-inch in a small beaker of distilled water. Continue boiling until no more air bubbles issue from the adapter tip. (Note 6.) (c) Without interrupting the distillation, remove the beaker of distilled water, and immerse the adapter to a depth of about a quarter-inch in 50 ml of 4% boric acid in the receiving flask. (Notes 7, 8.) (d) Through the funnel add slowly 40 ml of 6 *M* NaOH. (Note 9.) The screw clamp should always be closed except while NaOH is being added. Continue distilling at a brisk boil until about 75 ml of distillate have been collected. Then add slowly 20 ml more of 6 *M* NaOH, and collect 50 ml more of distillate. (Note 10.) Stop the distillation as follows: Lower the receiving flask until the adapter is out of the distillate. Collect another 5–10 ml of distillate, and then rinse the outside of the adapter with a little water from the wash bottle, adding the washings to the distillate. Then stop the heating. (Note 11.) (e) Add 6 drops of bromocresol green indicator to the distillate, and titrate with standard 0.1 *N* HCl. (Note 12.) (f) Perform a duplicate analysis on another 50-ml aliquot of sample solution. (Notes 13, 14.)

5. *Determination of the blank.* (Notes 15–17.) Perform duplicate blank determinations, using the same procedure as in step 4. In place of the sample solution, use a 50-ml portion of the same water that was used to dissolve the sample.

6. *Preparation of equipment for stand-by.* Remove the Kjeldahl flask, rinse, fill with about 100 ml of distilled water, and replace the flask. Let water drain from the condenser, as in step 3, and distill over about 30 ml of water. Rinse the adapter. Finally, rinse the Erlenmeyer and Kjeldahl flasks, and replace them.

7. *Calculations.* Find the average volume of standard acid required per 50-ml aliquot of sample solution, and correct for the blank. Calculate and report the % N in the sample.

NOTES

(1) These directions are for $(\text{NH}_4)_2\text{SO}_4$ - K_2SO_4 mixtures containing 80–100% $(\text{NH}_4)_2\text{SO}_4$. Show that a 50-ml aliquot of the sample solution requires about 30–45 ml of 0.1 *N* acid for titration. If other samples are used, the proper sample size and directions for preparation will be announced by the instructor.

(2) Boiled, carbonate-free water need not be used. Preserve a liter of the water for preparing samples for distillation, and for blanks. All solutions used in analysis

should be stored in stoppered bottles, to prevent contamination by NH_3 fumes from the atmosphere.

(3) It is recommended that the equipment be assembled by the instructor, and kept at a particular station in the laboratory. All new rubber connectors or stoppers should be boiled for 5 minutes in 20% NaOH and then rinsed thoroughly, to remove S- and N-containing organic compounds used in vulcanization. Connectors or stoppers that have been used previously and are in good condition do not need this treatment.

(4) The purpose of steaming out is to remove contamination. It is not necessary to do this before each run, or if the apparatus is clean. A steam out is desirable at the beginning of each day.

(5) The boiling chips prevent bumping, which causes surges of steam or air through the receiver solution, and which results in loss of NH_3 .

(6) The purpose of this operation is to drive off the air that fills the apparatus. If the air is not driven off in this way, the first portions of NH_3 come over in a stream of air that issues as fairly large bubbles from the adapter tip. These large bubbles pass through a very short length of absorbing solution, and NH_3 is not removed efficiently. Losses of several per cent may occur in this way.

(7) No NH_3 is lost in the boiling of the acid solution, and the beaker contents may be rejected.

(8) From this point, it is necessary to heat as evenly as possible. The flask, spray trap, and part of the condenser are filled with steam, and any fluctuations in rate of heating may cause the receiving-flask contents to be drawn up into the condenser, or may cause large bubbles to be ejected through the absorbing solution. To prevent accidental sucking up of the solution, the adapter tip is not immersed very deeply.

(9) Rapid addition of NaOH may cool the flask contents below boiling, drawing the receiving-flask contents into the condenser. Close the screw clamp while a little NaOH still remains in the funnel, to prevent air being drawn into the flask.

(10) It is helpful to put marks at the 125- and 175-ml levels on the receiving flask before distillation.

(11) If the burner is removed while the adapter is still immersed, the distillate may be sucked into the condenser.

(12) The basic color of bromocresol green is a pure blue. The end point is the appearance of a definite tinge of green. The end-point solution should be saved, so that the blank may be taken to the same color tint.

(13) The range of duplicates should be less than 0.08 ml for excellent work. If enough apparatus is available, it is well to set up two stills, so that the duplicates may be run in parallel.

(14) In the equipment described in this experiment, accuracy is sacrificed to some extent for simplicity and portability. The principal source of error is loss of NH_3 , either from loose connections or from incomplete absorption in the receiving flask. In practice, Kjeldahl analyses are performed in permanently installed equipment. In fact, unitized apparatus is commercially available in several designs. Multiple-unit installations exist that permit consecutive digestions and distillations of several samples. Much effort has gone into developing semi-micro- and microequipment, which is especially designed for rapid digestion and distillation and for complete recovery. In some equipment, ground glass joints are used. In most units uniform electrical heaters reduce bumping, both in digestion and distillation. In some units steam distillation is used to prevent bumping.

(15) The blank is always positive, and may be fairly large, owing to N in the re-

agents and distilled water, and to carry-over of NaOH as spray from the boiler. Blanks may be as high as 0.20 ml of 0.1 *N* HCl. The range of duplicate blanks should be less than 0.05 ml.

(16) The blank is best determined before the sample, so that the student may become familiar with the apparatus, and so that its cleanliness may be ascertained.

(17) If the analysis includes a digestion, the blank should be taken through the digestion step also. For the blank, an organic substance containing no N, such as N-free sucrose, is often used.

QUESTIONS

Section 18A

1. On separate plots, draw approximate curves for each of the following titrations. For each curve, indicate the substances present at various regions of the curve. Designate the equivalence-point volume, and indicate whether it falls in acid, neutral, or basic solution. (a) 100.0 ml of 0.1000 *M* NaOH with 0.2000 *M* HCl. (b) 50.00 ml of 0.1000 *M* HAc with 0.1250 *M* NaOH. (c) 80.00 ml of 0.05000 *M* NH₃ with 0.1000 *M* HCl.

2. In the curves for Figs. 18.2 and/or 18.3 (p. 345) explain: (a) the initial steep rise for a weak acid; (b) why, for a weak acid, the slope is at a minimum halfway to the equivalence point; (c) why the equivalence point is more basic the weaker the acid; (d) why the curve rises steeply near the equivalence point; (e) why the curves become coincident after the equivalence point.

3. Show roughly how the curves for the following two titrations lie with respect to each other, plotting both neatly on the same graph, so that they may be compared. (a) 500.0 ml of 0.01000 *M* HAc with 0.1000 *M* NaOH. (b) 50.00 ml of 0.1000 *M* HAc with 0.1000 *M* NaOH.

4. Draw the limiting curve for infinite dilution in Fig. 18.4 (p. 348). How does this curve depend upon K_a ?

5. Use a weak acid titration curve from Fig. 18.2 to support the statement (p. 323) that maximum buffering capacity exists when $[HA]/[A^-]$ is unity.

6. Suppose that a weak acid ($K_a = 1.0 \times 10^{-7}$ at 25°C) has a titration curve at 25°C as shown in Fig. 18.2. Show roughly how the curve at 100°C would lie with respect to the 25°C curve. (Assume that K_a is tenfold greater at 100°C than at 25°C. See Table 17.1 [p. 317] for K_w at 100°C.)

7. Why are the curves in Fig. 18.4 coincident before the equivalence point?

8. Draw neatly a pair of full-page axes for plotting titration curves. The vertical axis should run from pH 0–14. The horizontal axis should be marked at 0, 25, 50, and 100 ml. Draw a horizontal line at pH = 7, and vertical lines at 25, 50, and 100 ml. All curves and points requested should be put neatly on this plot and should be properly labeled.

(a) Draw a curve for the titration of 50.0 ml of 0.1000 *M* B ($K_b = 1.0 \times 10^{-5}$) with 0.1000 *M* HCl. Make no precise calculations, but indicate clearly about where the curve crosses the pH 7 line and the 0, 25, 50, and 100 ml lines. Label this curve *a*.

(b) Repeat *a*, with the difference that K_b is 1.0×10^{-7} . Label this curve *b*.

(c) Repeat *a*, with the difference that the 50-ml aliquot of base is diluted to 500 ml with water before beginning the titration. Label this curve *c*.

(d) Repeat *a*, with the difference that a 25-ml aliquot of base is used. Label this curve *d*.

9. Replot Fig. 18.5 (p. 349) roughly, giving pOH as ordinates instead of pH, and compare with Fig. 18.3.

10. On Fig. 18.3 or 18.5, pick out the curve that most closely describes the following titrations, and estimate the equivalence-point pH for each. (a) $0.10\ M\ NaBO_2$ with $0.10\ M\ HCl$. (b) $0.10\ M\ NaOCl$ with $0.10\ M\ HCl$. (c) $0.10\ M$ aniline hydrochloride with $0.10\ M\ NaOH$. (d) $0.10\ M$ ethanolamine hydrochloride with $0.10\ M\ NaOH$.

11. A 100.0-ml portion of $0.100\ M\ HA$ ($K_a = 1.0 \times 10^{-7}$) is titrated with $0.200\ M\ NaOH$. Without extensive calculations, draw an approximate titration curve, and label the equivalence-point pH and volume. On the same plot, show approximately how the curve would look at $100^\circ C$, where $K_a = 1.0 \times 10^{-6}$.

Section 18B

1. Explain why the color of an indicator does not change continuously throughout the pH range $0\text{--}14$.

2. From the indicator chart of Appendix VIII, select indicators for the titration of the acids shown in Fig. 18.3.

3. Why must the concentration of an acid-base indicator be kept low in a titration?

4. It is desired to estimate the pH of an unknown solution by comparing the color of an indicator in the unknown with the color of the same indicator in buffer solutions of known pH . What indicator would you choose for an unknown solution in each of the following pH ranges: (a) $2\text{--}4$; (b) $6\text{--}8$; (c) $10\text{--}12$?

5. Explain why methyl orange is not a good indicator for the titration of benzoic acid with standard $NaOH$. What indicators might properly be used? Describe the use of one of these indicators to secure maximum accuracy.

6. What indicators might be used in the following titrations with $0.1\ N$ solutions? (a) HCl with $NaOH$. (b) HAc with $NaOH$. (c) NH_3 with HCl . (d) Hydrazine with HCl .

7. Under what circumstances are indicators preferable to the pH meter?

8. Explain why the choice of end-point pH is not critically dependent upon titration conditions for the titration of a strong acid with a strong base but is quite critically dependent upon titration conditions for the titration of a rather weak acid with a strong base.

9. Suppose that K_I for a particular weak acid indicator is temperature independent. How will the pH limits of the transition range depend upon temperature? How will the pOH limits of the transition range depend upon temperature?

10. From data in Appendix VIII, describe the color changes of methyl violet.

Section 18C

1. By considering Fig. 18.3, verify the following statement: In $0.1\ N$ aqueous solutions, either HA may be titrated with $NaOH$, or NaA may be titrated with HCl , with a standard end-point error of only 1% or less, no matter what the value of K_a .

2. Explain how the normalities of the following solutions change in the storage reservoir on absorption of CO_2 from air: (a) Methyl orange normality of standard $NaOH$. (b) Phenolphthalein normality of standard $NaOH$. (c) Methyl orange normality of standard $Ba(OH)_2$. (d) Phenolphthalein normality of standard $Ba(OH)_2$.

3. Explain how $0.10\ M$ solutions of the following substances should be titrated with standard $0.10\ N$ acid or base, and select an indicator for each titration: (a) HAc , (b) methylamine, (c) hydroxylamine, (d) picric acid (yellow color), (e) tris (hydroxymethyl) aminomethane.

4. Explain why it should or should not be possible to titrate each of the following

substances accurately with strong acid or strong base in about 0.1 *N* solution: (a) formic acid, (b) aniline, (c) trimethylamine, (d) sodium benzoate, (e) HOCN.

5. Explain clearly the factors that contribute to the blank in the titration of HA with standard NaOH when the pH meter is used to establish the end point. Repeat the explanation when an indicator is used.

6. Why should a base solution be standardized to the same pH as the pH to which the base solution will be used in titrating sample solutions?

7. An NaOH solution contains carbonate, and its normality is determined by standardization against KHP with phenolphthalein. Describe the error, if any, in using this normality in the titration of (a) HCl, with methyl red indicator; (b) H_3PO_4 , with methyl orange indicator; (c) NaH_2PO_4 , with phenolphthalein indicator.

8. Explain what would happen if an airtight plug were used in Fig. 18.7 (p. 360) in place of the Bunsen valve, when the pressure in the system increases. How could such an increase in pressure occur in normal use and storage? Repeat answers for cases in which the pressure decreases.

9. In titration of an aliquot of 0.1 *M* HCl with 0.1 *M* NaOH, explain why an indicator like bromothymol blue (transition range, 6.0–7.6) would give a sharper end-point change than phenolphthalein or methyl orange if the solutions were perfectly free of carbonate. Explain why the bromothymol blue end point would be inferior if the solutions contained carbonate.

10. An aqueous solution of FeCl_3 is titrated with standard NaOH, using a pH meter to establish the point of maximum inflection. From the adsorption laws, predict how the calculated concentration of FeCl_3 would differ from the true concentration. Explain what might be done to decrease the error.

11. A worker must find the concentration of phenol in an aqueous solution containing nothing but water and phenol. Phenol is too weak to titrate directly and precisely with standard NaOH. Why could he not add an excess of standard NaOH to form sodium phenolate and then titrate the salt with standard HCl?

Section 18D

1. How does the titration curve for H_2SO_4 (Fig. 18.9, p. 362) differ from that for a strong acid such as HCl? How does it differ from the curve for a weak monoprotic acid, with $K_a = 10^{-2}$?

2. Write the equilibrium expressions for the ionization of tartaric acid. Explain why it is harder to calculate the pH of a tartaric acid solution than it is to calculate the pH of an H_3PO_4 solution.

3. Why cannot H_2O_2 be determined by titration with standard NaOH?

4. Is it practical to determine oxalic acid as a monoprotic acid? Why?

5. For the following mixtures, explain in each case why it is or is not possible to titrate the first substance in the presence of the second with fair precision. Select an indicator for each titration that is performable with fair precision. (a) HCl-HAc, (b) H_2SO_4 - HBO_3 , (c) HCl-HCN, (d) KHP- NaHCO_3 , (e) piperazine-pyridine, (f) ethylamine-sodium citrate, (g) hydrazine-aniline.

6. Outline the way in which each of the following substances may best be titrated with standard acid or base, when present alone in aqueous solution. Select an indicator for each titration that is performable with fair precision. (a) H_3AsO_4 , (b) H_2SO_3 , (c) citric acid, (d) salicylic acid, (e) ethylenediamine, (f) succinic acid, (g) glycine, (h) tyrosine, (i) EDTA (H_4Y).

7. Onto Fig. 18.9 sketch a rough curve for the titration of Na_2S with HCl.

8. Explain why more than two sharp end points are never observed in the titration of an aqueous solution containing two or more acids of different strengths.

The magnitude of this difference is much larger than that which should be obtained for excellent work (1 p.p.t.). List, with discussion, three of the more probable sources of error that would explain the observed difference.

7. Modify the instructions for Exp. 18.3 for the determination of the equivalent weight of a pure sample of an organic acid.

Experiment 18.4

1. In restandardizing the base according to step 3, the blank is negligible and is omitted. How might the negligibility of the blank be proved experimentally?

2. Describe the error in the reported P_2O_5 content, if the base is not restandardized, but its phenolphthalein normality is used.

3. Draw approximate curves for the following two titrations on a single plot in the region pH 3–10, so that the differences may be observed. (a) Titration of an aliquot of HCl with 0.1000 *N* base containing only NaOH and no Na_2CO_3 . (b) Titration of the same-sized aliquot of HCl with a standard base solution containing 0.1000 *M* NaOH, together with a small but significant concentration of Na_2CO_3 .

4. Repeat Ques. 3 for an aliquot of H_3PO_4 , instead of HCl.

5. What is the ratio of the volumes of standard base required to reach the pH 4–5 and pH 9–10 end points in the titration of H_3PO_4 , if the base (a) is carbonate-free, (b) contains a small but appreciable concentration of Na_2CO_3 ?

6. If the water used to prepare the H_3PO_4 sample contains an appreciable amount of CO_2 , what would be the error in H_3PO_4 content as calculated from (a) titration to the pH 4–5 end point, (b) titration to the 9–10 end point?

Experiment 18.5

1. Give the effect of each of the following mistakes on the calculated values of moles of HCl and moles of H_3PO_4 in the sample, assuming that no other mistakes are made in the analysis. (a) The normality of the acid used to restandardize the base is too low. (b) The standard base contains a rather high concentration of carbonate. (c) The HCl- H_3PO_4 sample contains an appreciable concentration of CO_2 . (d) In order to eliminate error due to CO_2 in the sample, the sample is boiled gently for a considerable time before titration. (e) Just one base normality (pH 4–5) is used for all computations. (f) A total of 34.00 ml of base is added to establish the first inflection point, which occurs at 31.90 ml. After the buret is refilled to the zero mark, titration to the second inflection point requires 35.98 ml more of base. The volume of base required to titrate the sample to the second inflection point is taken as 67.88 ml.

2. Draw an approximate titration curve for each of the following mixtures. (a) An equimolar mixture of HCl and H_3PO_4 . (b) A mixture containing slightly more HCl than H_3PO_4 . (c) A mixture containing slightly more H_3PO_4 than HCl.

3. When the base is titrated into the HCl- H_3PO_4 mixture, any carbonate in the base is converted to CO_2 , which may be lost to the atmosphere. This is particularly likely to happen at the beginning of the titration, when the solution is acidic. If a significant amount of CO_2 is lost in this way, give the effect, if any, on each of the following calculated quantities: (a) millimoles HCl plus millimoles H_3PO_4 , (b) millimoles HCl, (c) millimoles H_3PO_4 .

4. Describe techniques that might reduce the errors of Ques. 3.

5. A solution contains CO_2 , $HClO_4$, and H_3PO_4 . Describe how you would determine the concentration of each acid.

Experiment 18.6

1. In the digestion equation (p. 379), show that the first step is a hydrolysis, and the second a redox reaction.

2. Aluminum metal dissolves rapidly in conc. NaOH, with the violent evolution of hydrogen. Write the ionic equation. Speculate on the functions of the Zn and Cu in Devarda's alloy.

3. In the Marcali-Rieman method, when the formaldehyde is added to the solution of the ammonium salt at pH 5–6, the methyl red turns only orange, and not decidedly red. What does this show about the completeness of NH_4^+ conversion to hexamethylenetetramine and about the completeness of the liberation of H^+ ? Why does the reaction eventually go to completion?

4. Granulated zinc is sometimes added to the alkaline solution to prevent bumping in distillation. Describe the way in which Zn prevents bumping.

5. Give the effect, if any, of each of the following mistakes on the N content, as calculated in Exp. 18.6, assuming in each case that no other mistakes are made. (a) The standard acid normality is erroneously low. (b) The blank correction is not applied. (c) Some NaOH is carried into the sample distillate. (d) The acid sample is not boiled before base is added. (e) Methyl orange is used as an indicator instead of bromocresol green. (f) The NaOH used to liberate the NH_3 contains Na_2CO_3 .

6. Describe a simple procedure for the determination of NH_3 in an aqueous solution containing only NH_4Cl , NaNO_3 , and BaCl_2 .

PROBLEMS

Section 18A

1. Give the compositions of the solutions after the addition of 25.0, 50.0, and 55.0 ml of standard 0.1200 *M* NaOH to each of the following solutions: (a) 50.0 ml of 0.1100 *M* HAc, (b) 39.0 ml of 0.1400 *M* HAc, (c) 45.0 ml of 0.1300 *M* HAc diluted to 100.0 ml, (d) 6.50 meq HAc in 18.00 ml. Assume that volumes are additive.

Ans. (a) 0.0523 *M* NaAc and 0.0105 *M* NaOH, at 55.0 ml.

2. On the titration curve of Fig. 18.2 (p. 345), for $K_a = \infty$, calculate pH values when the following volumes of NaOH are added: 0.00, 30.00, 50.00, 55.00 ml.

3. Repeat Prob. 2 for $K_a = 10^{-6}$.

4. On the titration curve of Fig. 18.5 (p. 349), for $K_b = \infty$, calculate pH values when the following volumes of HCl are added: 49.60, 49.80, 50.00, 50.10 ml.

5. Repeat Prob. 4 for $K_b = 10^{-6}$.

6. Without altering the curves, relabel the axes for Fig. 18.3 (p. 345) to make this figure appropriate for titration of weak bases with K_b values equal to the K_a values shown for each curve. Discuss the relation between the resulting plot and Fig. 18.5.

7. What is the pH after the addition of 28.93 ml of 0.285 *M* NaOH to 48.93 ml of 0.193 *M* HCl?

Ans. 1.82

8. Repeat Prob. 7 if HA ($K_a = 1.00 \times 10^{-6}$) is used instead of HCl.

9. A 32.00-ml portion of 0.1345 *M* HAc is mixed with 39.00 ml of 0.0900 *M* NaOH. Calculate $[\text{H}_3\text{O}^+]$ and the pH.

Ans. 3.98×10^{-6} *M*; 5.40.

10. For the titration of the base B with HCl, derive relationships analogous to those in Ex. 4, page 348.

11. On the titration curve of Fig. 18.3, for $K_a = \infty$, what volume of base would correspond to pH 6.00? pH 8.00?

Ans. 49.999 ml; 50.001 ml.

12. In Ex. 1, page 346, show that the ionization of water contributes negligibly to $[\text{H}_3\text{O}^+]$, justifying the assumption that $[\text{H}_3\text{O}^+]$ is determined only by the HCl concentration.

13. Give the pH at the equivalence point when a 0.050 *M* solution of each of the following salts is titrated with 0.100 *M* HCl. (a) Na_2CO_3 (to form H_2CO_3), (b) NaBO_2 , (c) sodium acetylacetonate. *Ans.* (a) 4.03.

14. Calculate the end-point pH when 0.200 *M* NH_4Cl is titrated with 0.200 *M* NaOH. Explain why the end point is not sharp.

15. Calculate the end-point pH when 0.200 *M* NaAc is titrated with 0.200 *M* HCl. Explain why the end point is not sharp. *Ans.* 2.88.

16. Give the pH at the equivalence point when a 0.080 *M* solution of each of the following salts is titrated with standard 0.100 *M* NaOH. (a) aniline hydrochloride, (b) glycine hydrochloride, (c) imidazole hydrochloride, (d) hydroxylamine hydrochloride. *Ans.* (a) 8.64.

Section 18B

1. Select an indicator for each titration in Probs. 13 and 16, above, that is performable with fair precision.

Ans. Phenolphthalein for aniline hydrochloride (Prob. 16a).

2. An acid indicator changes from its basic color to its acidic color in passing from pH 8.3 to 6.1. What is the approximate value of pK_1 ?

3. The pH is 9.32 at the midpoint of the transition range of an indicator. At what pH would the indicator show its acid color? Its basic color?

Ans. 8.32; 10.32.

4. A difference from the pure acid color of an acid indicator may be detected when $[\text{In}^-]/[\text{HIn}]$ is 0.05 or more. Similarly, a difference from the pure basic color may be observed when $[\text{HIn}]/[\text{In}^-]$ is 0.02 or more. What is the magnitude of the transition range?

5. Assume that a one-color indicator behaves according to Eq. 18.2 (p. 353) and that the basic form, In^- , is the colored one. Assuming that the minimum $[\text{In}^-]$ detectable by the eye is 1.0×10^{-6} *M*, express $[\text{H}_3\text{O}^+]_{\text{acid color}}$ (i.e., the beginning of the transition range on the acid side) in terms of K_1 and the molar concentration (*C*) of the indicator. *Ans.* $(10^{\circ}\text{C} - 1)K_1$.

6. How would you prepare a comparison solution having the same pH as that at the equivalence point in the titration of malonic acid with standard 0.1000 *N* base? Pure malonic acid and sodium malonate are not available.

Section 18C

1. A 50.00-ml portion of 0.1000 *M* HCl is standardized with 0.1000 *M* NaOH. The indicator is a trace of bromophenol blue, which changes at pH 4.00. Calculate the (determinate) indicator error.

Ans. Calculated HCl concentration is 0.20% too high.

2. Using the titration curves of this chapter, estimate the standard error of the end point for each of the titrations of Probs. 13 and 16 (Sec. 18A), if indicators are used. *Ans.* 0.5% (Prob. 13a); 0.03% (Prob. 16a).

3. Calculate the standard error of the end point for each of the following titrations, if indicators are used. (a) 100.00 ml of 0.1000 *M* HAc with 0.2000 *M* NaOH. (b) 25.00 ml of 0.05000 *M* KHP with 0.02500 *M* NaOH, assuming that HP^- is a weak monoprotic acid and neglecting formation of H_2P . *Ans.* (b) 0.055 ml.

4. In the titration of a weak acid ($K_a = 10^{-7}$) with standard 0.10 *N* strong base, the indicator end point comes at pH 10.0, in a volume of about 100 ml. To determine a blank, a 100-ml sample of pure water containing the indicator is titrated and is found to require 0.13 ml of the base. Calculate the error of this experimental blank. Describe a better way to determine this blank.

5. Repeat Prob. 4, if $K_a = 10^{-5}$ and if the end point comes at pH 9.0.

Ans. 0.01 ml.

6. A 50.00-ml aliquot of a standard NaOH solution requires 46.30 ml of 0.1000 N HCl for titration to the methyl orange end point, and 46.10 ml to the phenolphthalein end point. What are the methyl orange and phenolphthalein normalities of the base solution? Assuming that the difference is due to carbonate in the base, give the composition of the base.

7. A 50.00-ml portion of 0.1000 N HA ($K_a = 1.0 \times 10^{-6}$) is titrated to a pH 9.50 end point with 0.1000 N NaOH, the following three techniques being used to establish the end point. (a) A pH meter. (b) Four drops (0.20 ml) of a 0.0040 M solution of a monoprotic acid indicator, added in the acid form, and half converted into the basic form at the end point. (c) Four drops of a 0.0040 M solution of a monoprotic acid indicator, added in the basic form, and 90% converted into the acid form at the end point. For each technique, calculate the determinate error of the end point.

Ans. (a) 0.016; (b) 0.020 ml.

8. Repeat Prob. 7, if a 10.00-ml portion of the HA solution is added to 90.00 ml of pure water, and then titrated by the three techniques.

9. The HA ($pK_a = 5.00$) concentrations in a series of samples may range from 0.0200 to 0.200 M . If 25-ml aliquots are titrated with 0.100 M NaOH, over what range may the equivalence-point pH fall? Choose an indicator.

Ans. 8.61–9.11; phenolphthalein.

10. Repeat Prob. 9, if $pK_a = 7.00$.

Section 18D

1. Verify the pH in the titration of H_3PO_4 under the conditions of Fig. 18.9 (p. 362), after 43.00 ml NaOH are added. After 94.00 ml NaOH are added.

2. Verify the pH in the titration of Na_2CO_3 under the conditions of Fig. 18.9, after 38.60 ml NaOH are added. After 99.50 ml NaOH are added.

3. What is $[H_3O^+]$ in the titration of 33.50 ml of 0.1500 M H_3PO_4 , after 30.00 ml of 0.1190 M NaOH are added? After 50.00 ml of 0.1190 M NaOH are added?

Ans. 0.00247 M (after 30.00 ml).

4. A solution contains 0.100 M HCl and 0.100 M HBO_2 . To what pH must the solution be titrated with a strong base in order to obtain the concentration of the HCl?

5. A solution is prepared by mixing 1.00 ml of 1.000 M HCl, 20.00 ml of 0.1000 M H_3PO_4 , 40.00 ml of 0.1000 M NaOH, and water to make 1.000 l. (a) What is the pH of the resulting solution? (b) Explain what effect a twofold dilution would have on the pH .

Ans. (a) 7.21.

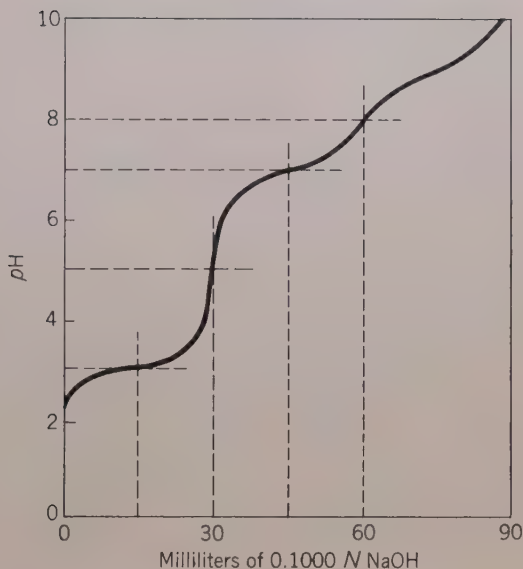
6. A 1.000-g sample of a single, pure acidic substance is made up to 100.0 ml with water, and titrated with 0.1000 N carbonate-free NaOH to give the titration curve on page 393. Tell as much as you can about the acid.

Experiments 18.1–18.3

1. By the procedure of Exp. 18.1, 2.0000 g Na_2CO_3 are dissolved, diluted to 250.3 ml, and a 50.00-ml aliquot is used to standardize an HCl solution. Calculate the concentration of the HCl solution, if 26.20 ml are required to titrate the aliquot directly.

Ans. 0.2880 N .

2. The Na_2CO_3 aliquot of Prob. 1 is titrated indirectly by adding 26.70 ml of the HCl to be standardized, boiling, and then back-titrating with NaOH (1.000 ml



NaOH = 1.100 ml HCl). If 0.46 ml of NaOH is required in back titration, what is the acid normality?

3. For the titration of Na_2CO_3 with standard HCl under the conditions of Fig. 18.10 (p. 369), the standard error between the equivalence-point pH and the end-point pH is 0.3 pH unit. Estimate the standard error of the end point in terms of milliliters of 0.1 M HCl. *Ans.* 0.2 ml.

4. By the method of Exp. 18.2, a one-fifth aliquot of a 1.300-g sample requires 38.26 ml of 0.0885 N HCl for titration. Compute the percentage of Na_2CO_3 in the sample as (a) Na_2CO_3 , (b) CO_2 .

5. What sample size should be used in Exp. 18.2, if the Na_2CO_3 content is 30–40%, and if it is desired to use 20–45 ml of 0.10 N HCl for titration? *Ans.* 1.8–3.0 g.

6. By the method of Exp. 18.3, a 2.800-g sample requires 47.82 ml of 0.1090 N NaOH for titration. Compute the percentage of KHP in the sample, assuming the blank to be zero.

Experiment 18.4

1. Describe the preparation of 2.0 l of an approximately 0.20 M H_3PO_4 solution, starting with conc. H_3PO_4 . *Ans.* Dilute 27 ml of conc. H_3PO_4 to 2.0 l.

2. Describe the preparation of 0.1000 ± 0.0001 M H_3PO_4 , starting with conc. H_3PO_4 .

3. What is the weight of P_2O_5 in a sample, a one-fifth aliquot of which requires 48.56 ml of 0.1000 N base for titration? *Ans.* 1.721 g.

4. What is the weight of H_3PO_4 in the sample of Prob. 3?

5. Derive a general equation analogous to that of Note 19 for the grams of H_3PO_4 in the unknown sample. *Ans.* Equation is the same as that of Note 19,

except that the factor $141.94/2$ is replaced by 97.99.

6. Suppose that it is desired to calculate the grams of P_2O_5 in the sample from the volume of base required to reach the second (pH 9–10, or Na_2HPO_4) end point. Derive a general equation similar to that of Note 19 for the grams of P_2O_5 in the whole sample. Explain how to determine the standard base normality that should be used in this calculation.

7. A 2.000-g sample contains 40.00% P_2O_5 , the rest being water. The sample is dissolved and made up to 250.0 ml. How much 0.2000 N carbonate-free $NaOH$ would be required for titration of a 50.00-ml aliquot to the methyl orange end point?

Ans. 11.27 ml.

Experiment 18.5

1. Calculate the millimoles of H_3PO_4 and the millimoles of HCl in a sample, a one-fifth aliquot of which requires 46.26 ml of standard base to the pH 4–5 end point and 29.75 ml more of the standard base from the pH 4–5 to the pH 9–10 end points. The pH 4–5 and pH 9–10 normalities of the base are 0.1006 and 0.0992 N , respectively.

Ans. 14.43 mmoles H_3PO_4 ; 8.84 mmoles HCl .

2. Calculate the grams of P_2O_5 and the grams of Cl in the sample of Prob. 1.

3. Explain the shape of your curve for restandardizing your base, in the region pH 4–10. Calculate the percentage difference between the pH 4–5 and pH 9–10 normalities. Assume that the difference is due to carbonate in the base, and calculate the $NaOH$ and Na_2CO_3 concentrations.

Experiment 18.6

1. The NH_3 from the digestion of 1.50 g of a protein sample is absorbed in 50.00 ml of 0.3000 N H_2SO_4 . Titration of the excess H_2SO_4 requires 11.35 ml of 0.2500 N $NaOH$. What is the % N in the sample?

Ans. 11.3%.

2. The NH_3 from the digestion of 2.10 g of a protein sample is absorbed in 5% HBO_2 . The NH_4BO_2 - HBO_2 solution requires 42.10 ml of 0.2396 N HCl for titration. What is the % N in the sample? Give the N content as % $(NH_4)_2SO_4$.

3. A 0.250-g sample of urea is digested and the NH_3 determined by the method of Exp. 18.6. How much 0.3280 N HCl is required for titration, assuming that the blank is zero?

Ans. 25.4 ml.

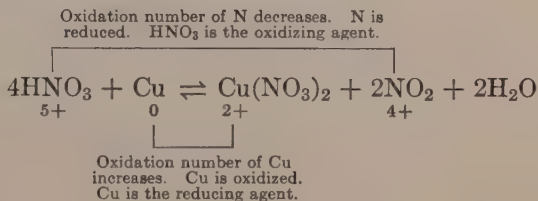
4. Nitrate in a KCl - $Al(NO_3)_3$ sample is reduced quantitatively to NH_3 in alkaline solution, and the NH_3 is distilled and recovered, according to Devarda's method. If the distillate requires 45.77 ml of 0.2200 N H_2SO_4 for titration, how many grams of $Al(NO_3)_3$ are in the sample? The blank is 0.22 ml H_2SO_4 .

19 REDOX STOICHIOMETRY AND EQUILIBRIA

19A. THE NATURE OF REDOX REACTIONS

19A.1. Definitions

A *redox* (i.e., oxidation-reduction) reaction is one in which the reacting substances undergo changes in oxidation number. The oxidizing agent becomes reduced, gaining electrons and decreasing in oxidation number. The reducing agent becomes oxidized, losing electrons and increasing in oxidation number. These definitions are illustrated in the following equation.



It is important to note that:

1. An *oxidizing agent* is an electron acceptor, and a *reducing agent* is an electron donor.
2. The redox process involves a transfer of electrons from the reducer (donor) to the oxidizer (acceptor). A reducer cannot give electrons unless an oxidizer is present to accept them. Thus reduction

never occurs alone to any appreciable extent, but is always accompanied by an equivalent amount of oxidation. The reagents react in such proportions that the number of electrons furnished by the reducer is exactly accepted by the oxidizer.

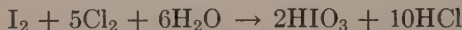
3. Without qualification, it is incorrect to consider a substance as being an oxidizer (or reducer). It is always necessary to refer to a certain *oxidation state* of that substance as being an oxidizer (or reducer). Thus in the above equation, Cu metal is a reducer; but Cu^{2+} could act as an oxidizer, since it is capable of going to a lower oxidation state. The oxidized and reduced forms of a substance may be regarded as interconvertible, and are called a *redox conjugate pair*. The chemical equation for the interconversion is called a *half-reaction*:



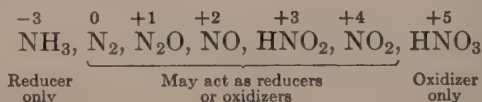
4. An element in an intermediate oxidation state is theoretically capable of acting either as an oxidizer or a reducer. How it acts depends on the relative oxidizing or reducing strength of the other reacting substance. As an example, elemental iodine may act as an oxidizer if mixed with a strong reducer, such as H_2SO_3 .



On the other hand, if elemental iodine is mixed with a considerably stronger oxidizer such as elemental chlorine, the iodine acts as a reducer.



Other elements behave similarly. Thus N possesses the following common oxidation states.



5. If it is desired only to designate the oxidation state of an element, with no commitment as to the actual form in which that element exists, then parenthetical roman numerals are used. Thus Ce(IV) denotes quadrivalent Ce. (The reader must supply the sign.) This designation is often sufficient. If it is desired to indicate the forms in which the element exists, it is best to use the chemical formulae. For example, Ce(IV) may exist in a particular solution as hydrated Ce^{4+} , as complexed $\text{Ce}(\text{NO}_3)_6^-$, or perhaps in a partially hydrolyzed form, such as $\text{Ce}(\text{OH})(\text{NO}_3)_5^-$.

19A.2. The Extent of Redox Reactions

Oxidizing agents may be arranged in the order of their tendency to accept electrons. Such an arrangement, called the *table of standard potentials* (TSP), is given in Appendix IX (p. 930). In this table, oxidizing agents are placed on the left and reducing agents on the right. Oxidizers high in the table are strong ones and show a relatively strong tendency to go to the reduced forms. Reducing agents low in the table are strong ones and show a relatively great tendency to go to the oxidized forms.

In general, if an oxidizing agent lies above a reducing agent by several tenths of a volt, they tend to react rather completely when mixed, and the equilibrium lies far on the side of the products. On the other hand, if a reducing agent lies above an oxidizer by several tenths of a volt, the reaction tendency between them is slight, and the equilibrium lies far on the side of the reagents. If a reducer and an oxidizer lie at about the same level in the table, they tend to react when mixed, but appreciable amounts of both products and reagents exist at equilibrium. Figure 19.1 summarizes these statements.

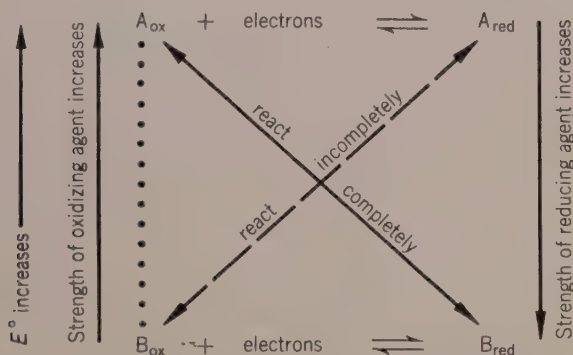
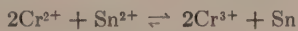


FIG. 19.1. Plan of the Table of Standard Potentials

Example 1. The oxidizer Sn^{2+} (at -0.136 v) reacts quite completely with the reducer Cr^{2+} (at -0.41 v):



Although the reverse reaction can also occur (i.e., Cr^{3+} can oxidize Sn metal), the extent is negligible. The equilibrium lies predominantly to the right because Sn^{2+} is a stronger oxidizer than Cr^{3+} .

Example 2. The oxidizer VO_2^+ (at 1.00 v) is reduced very completely to VO^{2+} by Sn^{2+} (at 0.15 v). The product, VO^{2+} (at 0.361 v), is also an oxidizer, and can be further reduced to V^{3+} by Sn^{2+} , provided that there is enough of the latter. However, V^{3+} (at -0.255 v) is not appreciably reducible to V^{2+} by Sn^{2+} , since Sn^{2+} is a

weaker reducer than V^{2+} . The unbalanced reaction between VO_2^+ and excess Sn^{2+} is, therefore,



The foregoing statements regarding completeness of reaction are given at this point as an introduction to the general scheme and uses of the TSP. But actually, these statements are only rough generalizations; further considerations are necessary, and are presented in Secs. 19D–F (pp. 404–27).

The TSP is extremely valuable, for it summarizes much descriptive inorganic chemistry that would otherwise have to be memorized. The nature of the products, as well as the extent of the reaction, may be deduced from the TSP, and such knowledge may be used to write and balance redox equations.

Appendix IX is an abbreviated form of the TSP, and contains only those half-reactions that are pertinent to the subjects of this book. More extensive versions may be found in the literature (L6).

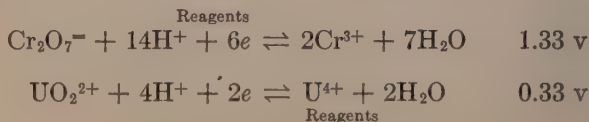
19B. BALANCING REDOX EQUATIONS

There are several systematic procedures for balancing redox equations, but all are based upon the principle that the reducer and oxidizer react in such proportions that the electrons given off by the reducer are exactly accepted by the oxidizer.

The *method of the skeleton*, or *over-all equation* (B15), is taught in most first-year chemistry courses, and should be reviewed at this point. It is particularly useful when the products of the reaction are known.

A very systematic procedure, called the *method of half-reactions*, is based upon the TSP, and is of great utility in analytical chemistry. The method of half-reactions is outlined stepwise below, illustrated by the oxidation of U^{4+} with $Cr_2O_7^{2-}$ in acid solution.

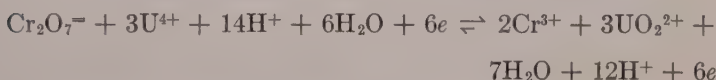
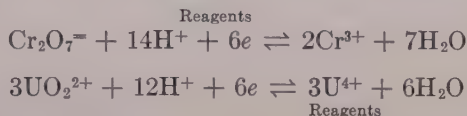
1. Write the half-reactions involving the reagent substances, being careful to preserve the identity of the reagents. In the U^{4+} - $Cr_2O_7^{2-}$ reaction, the half-reactions are found in the TSP.*



Since there is a large difference between the E° values, the reaction tendency is high, and the equilibrium lies far on the side of the products.

*To conform with most standard treatments of redox theory, the hydronium ion is written as H^+ instead of more properly as H_3O^+ .

2. Multiply each half-reaction through by an integer, so that the same number of electrons is involved in each half-reaction. To obtain the over-all reaction, simply combine the reagent sides of both half-reactions, and then combine the product sides. For the U^{4+} - Cr_2O_7^- reaction,



3. To obtain the final equation, cancel the electrons, which are always equal on both sides of the over-all equation, and combine or cancel like molecules or ions.

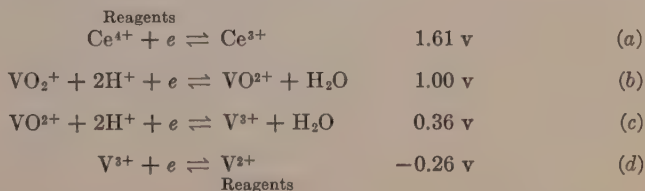


4. Check: Ascertain that the various types of atoms (and the net charge) balance on both sides of the equation. If a balance is not obtained, an arithmetical error should be sought.

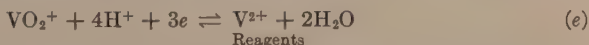
In the preceding illustration, only two half-reactions are involved, and there is no question about the nature of the products. However, this is not always the case. Judgment is sometimes required to decide which are the correct half-reactions and products, as shown in the following examples.

Example 1. Write the equation for the action of excess Ce^{4+} on V^{2+} .

Inspection of the TSP shows that Ce^{4+} is strong enough to oxidize V^{2+} not only to V^{3+} , but also to oxidize the V^{3+} in turn through VO^{2+} to VO_2^+ . The pertinent half-reactions are:



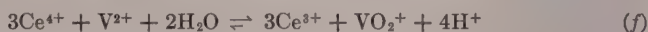
The resultant half-reaction for V^{2+} going to VO_2^+ may be obtained by summing Eqs. b, c, and d, so that V^{3+} and VO^{2+} cancel out:



The resultant equation of course has an E° value that is not of use in balancing equations, but that is of use in other applications. The calculation of E° for a re-

sultant half-reaction is described in the Supplement (p. 807). Sometimes, tables may contain resultant half-reactions as well as stepwise ones. (See Appendix IX for Cu.)

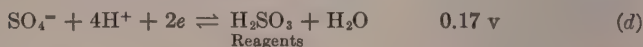
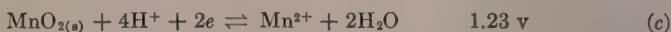
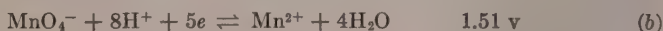
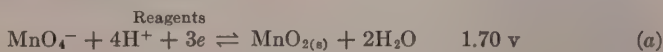
After multiplying Eq. *a* by 3, combination of the reagent and product sides of Eqs. *a* and *e* gives the desired over-all equation.



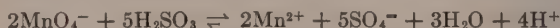
Example 2. Write the equation for the action of excess H_2SO_3 on MnO_4^- in acid solution.

The TSP gives two seemingly contradictory half-reactions in which MnO_4^- acts as an oxidant, Mn^{2+} being produced in one case and MnO_2 in the other.

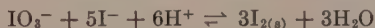
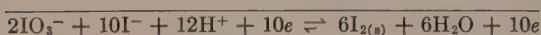
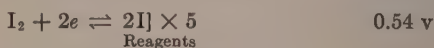
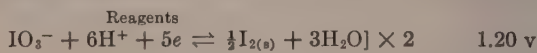
Pertinent half-reactions are:



However, H_2SO_3 is capable of reducing MnO_2 further to Mn^{2+} , and the net result is the same whether one conceives the reduction of MnO_4^- to occur via Eq. *b*, or via Eqs. *a* and *c*. The balanced equation is

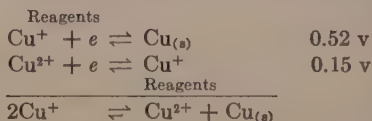


Example 3. Write the equation for the reaction between IO_3^- and I^- in acid solution.



In this example, both IO_3^- and I^- go to the same oxidation state (elemental iodine), but this causes no difficulty in the balancing procedure.

Example 4. Write the equation for the autoxidation (i.e., disproportionation) of cuprous ion.



Cuprous ion is thus highly unstable, according to the TSP, and spontaneously disproportionates to other oxidation states.

Disproportionation is not unique to copper. Any element in an intermediate oxidation state tends to disproportionate, but the extent is slight if the intermediate state is stable. For example, there is a very slight tendency for iodine to decompose to I^- and IO_3^- , according to the reverse of the reaction in Ex. 3, above.

An abbreviated TSP (like Appendix IX) may not contain the half-reaction needed to balance the equation for a particular reaction. In such a case, if the chemistry is known, a half-reaction may be formulated.

Example 5. Write the equation for the reduction of plutonyl ion (PuO_2^{2+}) by a metallic Zn reductor in acid solution. Metallic Zn reduces plutonium to Pu^{3+} .

The half-reaction for Zn acting as a reducing agent may be found from the TSP.



The PuO_2^{2+} - Pu^{3+} half-reaction cannot be found in the TSP, so it must be formulated as follows:

(a) Find the change in oxidation number of the element (Pu), and add this number of electrons to the left (oxidized) side of the half-reaction. In PuO_2^{2+} , the oxidation number of Pu is +6,* while in Pu^{3+} , it is +3. The change in oxidation number is 3, and the unbalanced half-reaction is

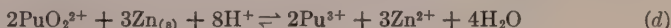


(b) For any unbalance in oxygen that may exist, add H^+ to form H_2O in acid solution, or H_2O to form OH^- in basic solution. The balanced PuO_2^{2+} - Pu^{3+} half-reaction is



(c) Check: Find if the charges balance. A net charge of +3 on the left side just balances the charge of +3 on the right. If a balance is not obtained, an arithmetical error should be sought.

Combination of the two balanced half-reactions *a* and *c* gives the balanced over-all equation.



19C. REDOX STOICHIOMETRY

In redox titrations, concentrations may be expressed in terms of *molarity*, *titer* value, or (redox) *normality*.

In general, there are *n* equivalents per mole of an oxidizing or reducing agent, where *n* is the number of electrons donated or accepted by one molecule of the agent. The behavior of the substance in the TSP gives *n* directly, or it may be calculated from the change in oxidation number of the element. The (redox) *equivalent weight* is equal to the molecular weight or some submultiple of it.

*If the oxidation number of a particular atom is not known, it may be deduced from the known oxidation numbers of other atoms associated with it in the ion or molecule. Thus, if the oxidation number of Pu in PuO_2^{2+} is not known, it may be deduced as follows:

$$\left(\begin{array}{c} \text{Charge on} \\ \text{Pu in } \text{PuO}_2^{2+} \end{array} \right) + \left(\begin{array}{c} \text{charge on} \\ \text{two O's, or } 4- \end{array} \right) = \left(\begin{array}{c} \text{charge on} \\ \text{PuO}_2^{2+}, \text{ or } 2+ \end{array} \right)$$

From this equation, the charge on Pu may be calculated as 6+. In some cases ($\text{S}_2\text{O}_8^{2-}$, Fe_3O_4 , etc.), the oxidation number of an element may be a fraction. Such a fraction represents an average for all atoms of that element in the molecule. The balancing procedure described above is applicable without modifications to equations involving fractional oxidation numbers.

$$\text{Equivalent weight} = \frac{\text{molecular weight}}{n} \quad (19.2)$$

$$\text{Equivalents} = \frac{\text{grams}}{\text{equivalent weight}} \quad (19.3a)$$

or

$$\text{Milliequivalents} = \frac{\text{milligrams}}{\text{equivalent weight}} \quad (19.3b)$$

The (redox) normality, N , is a concentration unit, expressing the number of equivalents of an oxidizing or reducing agent per liter of solution.

$$\text{Normality} = \frac{\text{equivalents of solute}}{\text{liters of solution}} = \frac{\text{milliequivalents of solute}}{\text{milliliters of solution}} \quad (19.4)$$

There is no general relation between redox and acid-base equivalents. Also, the terms "equivalents" and "normality" are usually used without modifiers, and it is necessary to decide from the context whether redox or acid-base quantities are implied. There tends to be ambiguity in the use of redox equivalents and normality, since some redox agents may react in more than one way. In order that redox equivalents and normality may make sense, the chemical equation by which the substance reacts must be explicitly stated, or understood from the context.

Table 19.1 should clarify the above definitions. It should be noted that the term "1 N KMnO_4 " out of context is ambiguous, for it may mean 1 M , 0.33 M , or 0.20 M ; only when a particular reaction is associated with the term does it become definite.

TABLE 19.1

RELATION OF EQUIVALENT WEIGHT TO MOLECULAR WEIGHT, AND OF NORMALITY TO MOLARITY

Substance	Unbalanced Reaction	Equivalents per Mole (n)	Equivalent Weight (MW/n)	1 M Solution Is
CuSO_4	$\text{Cu}^{2+} \rightarrow \text{Cu} \downarrow$	2	$\text{MW}/2$	2 N
KMnO_4	$\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$	5	$\text{MW}/5$	5 N
	$\text{MnO}_4^- \rightarrow \text{MnO}_2 \downarrow$	3	$\text{MW}/3$	3 N
	$\text{MnO}_4^- \rightarrow \text{MnO}_4^{2-}$	1	MW	1 N
$\text{K}_2\text{Cr}_2\text{O}_7$	$\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$	6	$\text{MW}/6$	6 N
$\text{H}_2\text{C}_2\text{O}_4$	$\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CO}_2$	2	$\text{MW}/2$	2 N

The usefulness of the concepts of redox equivalents and normality lies in the fact that one equivalent of a sought-for substance always requires for titration one equivalent of the standard reagent; thus computations may be made without balancing the chemical equations for the reactions involved in the determination.

$$\left(\begin{array}{c} \text{Equivalents of sought-} \\ \text{for substance} \end{array} \right) = \left(\begin{array}{c} \text{equivalents of} \\ \text{standard reagent} \end{array} \right) \quad (19.5)$$

These concepts are applied in the following illustrative examples. These examples could, of course, be done with moles and molar concentrations.

Example 1. A sample of $\text{H}_2\text{C}_2\text{O}_4$ requires 10.00 ml of 0.1002 N KMnO_4 for titration. How many grams of $\text{H}_2\text{C}_2\text{O}_4$ are in the sample?

When $\text{H}_2\text{C}_2\text{O}_4$ reacts with permanganate, CO_2 is formed. (See TSP.)



There are therefore 2 eq per mole of $\text{H}_2\text{C}_2\text{O}_4$, and the equivalent weight is one-half of the molecular weight. The weight of $\text{H}_2\text{C}_2\text{O}_4$ may now be calculated.

$$0.1002 \times 10.00 \left| \begin{array}{l} \times \frac{90.04}{2} \\ \hline \text{mg H}_2\text{C}_2\text{O}_4 \\ \hline \text{meq KMnO}_4, \text{ or meq H}_2\text{C}_2\text{O}_4 \end{array} \right| = 45.11 \text{ mg}$$

Example 2. The Fe content of a 2.500-g ore sample is to be reported as Fe_3O_4 . All Fe is extracted and reduced quantitatively to Fe(II) , which is then titrated with 0.1063 N KMnO_4 , 25.27 ml being required. Calculate the Fe content as % Fe_3O_4 .

Each Fe in the original Fe_3O_4 is processed to give one Fe(II) . In turn, each Fe(II) shows 1 eq per mole when oxidized to Fe(III) by the KMnO_4 . Therefore there are 3 eq per mole of Fe_3O_4 .

The weight of Fe_3O_4 may now be calculated.

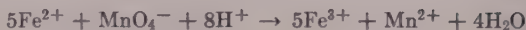
$$0.1063 \times 25.27 \left| \begin{array}{l} \times \frac{231.54}{3} \\ \hline \text{mg Fe}_3\text{O}_4 \\ \hline \text{meq KMnO}_4 = \text{meq Fe}_3\text{O}_4 \end{array} \right| \times \frac{100}{2500} = 8.29\%$$

Example 3. What is the Fe_3O_4 titer of the KMnO_4 solution of Ex. 2?

$$0.1063 \times 1 \left| \begin{array}{l} \times \frac{231.54}{3} \\ \hline \text{mg Fe}_3\text{O}_4 \text{ equivalent to 1 ml} \\ \hline \text{meq KMnO}_4 \text{ in 1 ml, or meq Fe}_3\text{O}_4 \\ \text{equivalent to 1 ml} \end{array} \right| = 8.20 \frac{\text{mg Fe}_3\text{O}_4}{\text{ml}}$$

Example 4. The use of normal concentrations may become confusing when the standard solution is standardized and used by different reactions. In such cases, it is better to work through moles, rather than equivalents, as this example shows.

(a) A KMnO_4 solution is standardized by titration against a standard FeSO_4 solution. Calculate the normality of the KMnO_4 solution, if 25.25 ml are required to titrate a 25.00-ml portion of 0.1000 N FeSO_4 according to the reaction



$$0.1000 \times 25.00 \left| \times \frac{1}{25.25} \right| = 0.0990 \text{ N KMnO}_4$$

$\left| \begin{array}{l} \text{meq KMnO}_4 \text{ per ml} \\ \text{meq FeSO}_4, \text{ or meq KMnO}_4 \text{ in } 25.25 \text{ ml} \end{array} \right|$

(b) Calculate the concentration of an MnSO_4 solution, 25.00 ml of which require 25.75 ml of the 0.0990 N KMnO_4 for titration according to the Volhard reaction for determining Mn(II) .



The concentration of the MnSO_4 solution *cannot* be calculated by assuming that 1 eq of MnO_4^- reacts with 1 eq of Mn(II) , and that therefore the normality of the MnSO_4 is

$$0.0990 \frac{25.75}{25.00} = 0.1020 \text{ N}$$

The reason for this restriction is that permanganate shows 5 eq per mole in the standardization reaction of part a, but only 3 eq per mole in the reaction of part b.

One way to solve this problem is as follows:

$$\text{Molarity of KMnO}_4 (\text{from part a}) = \frac{0.0990}{5} = 0.01980 \text{ M}$$

$$0.01980 \times 25.75 \left| \times \frac{3}{2} \times \frac{1}{25.00} \right| = 0.03059 \text{ M MnSO}_4$$

$\left| \begin{array}{l} \text{mmoles MnSO}_4/\text{ml} \\ \text{mmoles MnSO}_4 \text{ in } 25.00 \text{ ml} \\ \text{mmoles KMnO}_4 \text{ used} \end{array} \right|$

19D. REDOX EQUILIBRIA

The theory presented in this section is necessary for an understanding of the very important and large group of electrochemical methods of analysis, including titrations and electrodepositions.

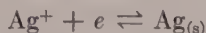
19D.1. Attainment of Redox Equilibrium

As a redox reaction proceeds, the oxidizer is used up and its concentration diminishes, decreasing its oxidizing power. Similarly, as the reducer is used up, its concentration decreases and so does its reducing power. Eventually, a point is reached where the power of the remaining oxidizer is insufficient to take electrons from the reducing agent; then reaction ceases and equilibrium exists. At equilibrium, the proportions of original reducer and original oxidizer that are still left de-

pend on how far apart these two substances lie in the TSP; the farther apart, the greater the extent of reaction, and the smaller the amounts of original oxidizer and reducer left at equilibrium. This process is described quantitatively in the following sections.

19D.2. The Single-Electrode Potential

19D.2a. The single-electrode potential as a measure of oxidizing strength. When an Ag electrode is dipped into a solution of AgNO_3 , there is a tendency for the Ag to plate out onto the electrode:



Ag^+ ions tend to absorb electrons from the electrode,* and to be converted to Ag metal. This process leaves the electrode positively charged relative to the solution, which is negatively charged by the NO_3^- left behind. An appreciable potential difference thus tends to be developed between the positive electrode and the negative solution. However, as the potential builds up, electrons become more difficult to extract from the electrode, and the process reaches equilibrium. The extent of chemical reaction required to give the potential (of the order of a few volts) is negligible, and the concentration of Ag^+ in solution is diminished imperceptibly. (See footnote, p. 187.) The process should be regarded as a tendency, rather than an actual reaction that occurs appreciably.

The greater the tendency of Ag^+ to go to Ag, the greater is the potential built up between the electrode and the solution. This potential, called the *single-electrode potential* (E), is therefore related to the tendency of Ag^+ to go to Ag, and may be taken as a measure of the oxidizing strength of the system.

It should be recognized that the reverse tendency also exists. That is, there is a tendency for Ag metal to dissolve to give Ag^+ , which process makes the electrode negative with respect to the solution. The potential built up is greater the greater the tendency for Ag to go to Ag^+ , and may therefore be taken as a measure of the reducing strength of the system. Whether the oxidation or reduction tendency is greater, and whether the electrode tends to be negatively or positively charged with respect to the solution, depends upon the chemical nature of the system and the concentrations of the solute species present, as described below.

The E cannot be measured directly, and absolute values are not known. However, differences between two E 's may be measured, so that the E 's for all systems are known relative to each other. The E 's in the table of standard potentials are such relative values, the E of the

*Electrons, unlike ions, cannot exist in solution, but can exist and be transferred only at the surface of a conductor.

H^+-H_2 half-reaction being taken as zero. Systems with a high E are much more strongly oxidizing than systems containing H^+-H_2 , while systems with a negative E are much more strongly reducing.

19D.2b. Dependence of E on concentration. The Nernst equation. Suppose that the half-reaction describing a particular system is



It may be seen that any increase in concentration of A_{ox} or B , or any decrease in concentration of A_{red} or D forces the equilibrium to the right and increases the oxidizing strength of the system. The oxidizing strength of the system therefore depends not only on the concentrations of the oxidized and reduced species, but also upon the concentrations of the other reacting species. Through the Nernst equation, E is quantitatively calculable from the composition of the system, and is a quantitative measure of the oxidizing power of the system.

The dependence of E upon the concentrations of the species involved in the half-reaction is given by the Nernst equation,

$$E = E^\circ + \frac{0.0591}{n} \log \frac{Q_{ox}}{Q_{red}} \quad (19.7)$$

E is the single-electrode potential of the system. The larger E is, the greater is the oxidizing power.

E° is the standard single-electrode potential of the system.

0.0591 is a constant at $25^\circ C$. More generally, this constant is $(RT/F) \log_e 10$. R is the gas constant, 8.314 joules per $^\circ C$. T is the absolute temperature, 298° . F is the Faraday, 96,500 coulombs per equivalent. $\log_e 10$ is 2.303.

n is the number of electrons involved in the half-reaction.

Q_{ox} and Q_{red} are the mass-action expressions for the oxidizing and reducing sides of the half-reaction, respectively, written in accord with certain conventions.* As an example, Q_{ox}/Q_{red} for Eq. 19.6 is

$$\frac{[A_{ox}][B]^b \cdots}{[A_{red}][D]^d \cdots} \quad (19.8)$$

*These conventions are summarized here. (1) For any soluble species i , $[i]$ is its molar concentration. (2) An insoluble solid or liquid substance saturating the solution has a fixed concentration and is omitted from the mass-action expression. (3) The concentration of a gaseous substance in equilibrium with the system could be expressed as a molar concentration. However, the concentration of a gas in solution is approximately proportional to its partial pressure over the solution, so that the mass-action effect of a gaseous solute is more conveniently expressed in terms of its pressure (atmospheres) rather than in terms of its molar concentration.

For exact work, activities should be used instead of molar concentrations, as shown in the Supplement (p. 808). As originally formulated by Nernst, the expression contained molarities, since the concept of activities had not yet been invented. For elementary analytical purposes, the activity of a solute species may be considered to be the same as its molarity. This approximation is made in all the illustrative examples of the elementary section of this book.

19D.2c. The standard single-electrode potential (E°). The standard single-electrode potential (E°) is E when all species involved in the mass-action expressions Q_{ox} and Q_{red} are at certain standard activities. Such a system and the substances therein are said to be at the *standard state*. Standard-state activities are defined differently for different types of solutes. A soluble substance is at its standard state when its activity is 1 M . A dissolved gas is at its standard state when its partial pressure over the solution is 1 atmosphere. The standard state of an insoluble liquid or solid substance is the saturated solution. At the standard state the log term in Eq. 19.7 is zero, and $E = E^\circ$.

The E° value is therefore a measure of the oxidizing power of a particular system in which all species involved in the half-reaction are at their standard states, and the systems of Appendix IX are listed in this order. If any solute species for a particular system is at an activity other than standard, the oxidizing power (i.e., E) is different from E° , and is calculable from the Nernst equation.

As with E , absolute E° values are not known. The E° values of Appendix IX are relative to the E° for the $2\text{H}^+ + 2e \rightleftharpoons \text{H}_2$ half-reaction, which is taken as zero. In order to avoid confusion regarding standard states, soluble substances are given in the predominant form in which they exist in solution, gases are denoted by the subscript (g), and insoluble solids and liquids are denoted by the subscripts (s) and (l).

19D.2d. Computation of E

Example 1. Write expressions for the E of several systems in Appendix IX.

$$\text{Zn}^{2+} + 2e \rightleftharpoons \text{Zn}_{(s)} \quad E = -0.763 + \frac{0.0591}{2} \log [\text{Zn}^{2+}]$$

$$\text{AgI}_{(s)} + e \rightleftharpoons \text{Ag}_{(s)} + \text{I}^- \quad E = -0.151 + 0.0591 \log \frac{1}{[\text{I}^-]}$$

$$\text{MnO}_4^- + 8\text{H}^+ + 5e \rightleftharpoons \text{Mn}^{2+} + 4\text{H}_2\text{O} \quad E = 1.51 + \frac{0.0591}{5} \log \frac{[\text{H}^+]^8 [\text{MnO}_4^-]}{[\text{Mn}^{2+}]}$$

$$\text{O}_{3(g)} + 2\text{H}^+ + 2e \rightleftharpoons \text{O}_{2(g)} + \text{H}_2\text{O} \quad E = 2.07 + \frac{0.0591}{2} \log \frac{[\text{H}^+]^2 (P_{\text{O}_3})}{(P_{\text{O}_2})}$$

Example 2. Calculate E for 0.010 M HNO_3 saturated with oxygen at a partial pressure of 0.20 atm, and with ozone at a partial pressure of 0.00010 atm. Use the expression in Ex. 1.

$$E = 2.07 + \frac{0.0591}{2} \log \frac{(0.010)^2 (0.00010)}{(0.20)} = 1.85 \text{ v}$$

After a numerical value is obtained for E , it should be examined to ascertain that it is reasonable. In this example, both O_3 and H^+ are far below their standard concentrations, while O_2 is only slightly below. This system is therefore less strongly

oxidizing than the standard system, and E should be lower than E° . Arithmetical errors should be sought for answers that appear to be unreasonable.

19D.2e. Effect of precipitation, complexing, and pH on E . As already mentioned, if any of the species involved in a half-reaction is precipitated, complexed, or otherwise removed, the oxidizing power and E are changed. The nature and extent of the changes may be large, as shown in the following examples.

Example 1. E° for the Ag^+ -Ag half-reaction is 0.799 v. What is E if excess KI is added to bring $[\text{I}^-]$ to 1.00 M , so that $[\text{Ag}^+]$ is reduced much below its standard-state concentration, owing to the formation of AgI ?



If $[\text{I}^-] = 1.00 M$, $[\text{Ag}^+]$ may be calculated from the solubility product of AgI .

$$[\text{Ag}^+] = \frac{K_s}{[\text{I}^-]} = \frac{9.8 \times 10^{-17}}{1.00} = 9.8 \times 10^{-17} M$$

$$E = 0.799 + 0.0591 \log (9.8 \times 10^{-17}) = -0.148 \text{ v}$$

Thus in the presence of 1 M iodide the oxidizing power of the Ag^+ -Ag system is much lower than when $[\text{Ag}^+] = 1 M$. The reducing power of metallic Ag is increased by the presence of the iodide.

Inspection of Appendix IX shows the half-reaction



This E° is practically identical with the E calculated above. In order to save computation, many other such half-reactions for the behavior of a given element in different media are listed in the TSP. (See E° values for the Ag^+ -Ag half-reaction in the presence of cyanide, bromide, and chloride.)

Conversely, if the E° of a system is known, and if the E of the system is then measured in the presence of a known concentration of a precipitating agent, the solubility product may be calculated. Stability constants for complex formation and ionization constants for weak acids and bases may be similarly calculated (p. 421). Electrochemical measurements are therefore very important in the determination of equilibrium constants.

Example 2. Calculate E for a system containing O_2 and O_3 at 1.00 atm each, when $[\text{OH}^-]$ is 1.00 M .

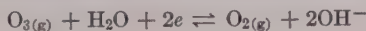


$$E = 2.07 + \frac{0.0591}{2} \log \frac{[\text{H}^+]^2(P_{\text{O}_3})}{(P_{\text{O}_2})}$$

In basic solution $[\text{H}^+]$ is very low, and the oxidizing strength of ozone is greatly diminished. When $[\text{OH}^-]$ is 1.00 M , $[\text{H}^+]$ is $K_w/[\text{OH}^-]$, or $1.01 \times 10^{-14} M$. Therefore

$$E = 2.07 + \frac{0.0591}{2} \log \frac{(1.01 \times 10^{-14})^2(1.00)}{(1.00)} = 1.24 \text{ v}$$

Since this E is for a system containing O_2 , O_3 , and OH^- at standard concentrations, it is also the standard single-electrode potential (i.e., E°) for the half-reaction



This half-reaction is also listed in Appendix IX.

This example reveals a point of great practical importance, especially in biochemical systems: namely, that the oxidizing strengths of many systems may be easily controlled by controlling the pH.

19D.2f. Formal single-electrode potentials. Because of activity and complexing effects, it might be very misleading to take E° as a measure of the oxidizing power of a given redox pair in all different kinds of media. For example, E° for the Cr(VI)-Cr(III) half-reaction is given as 1.33 v, and the E in a system containing 1.00 M HCl, 0.00133 M $K_2Cr_2O_7$, and 0.00133 M $CrCl_3$ might be estimated as

$$\begin{aligned} 1.33 + \frac{0.0591}{6} \log \frac{[Cr_2O_7^{2-}][H^+]^{14}}{[Cr^{3+}]^2} &= 1.33 + \frac{0.0591}{6} \log \frac{(0.00133)(1.00)^{14}}{(0.00133)^2} \\ &= 1.36 \text{ v} \end{aligned}$$

Chloride should be oxidizable in this system, since E° for Cl_2-Cl^- is 1.36 v. But actually, chloride is not oxidizable by dichromate at moderate acidity, and an experimental measurement of E for the above dichromate system gives a value of only 1.09 v.

To avoid such difficulties, there are available formal E 's, some of which are given in Appendix IX. A more complete list is given by Swift (S36). A *formal E* is an E in a system containing low and equivalent (unless otherwise specified) formal concentrations* of the oxidized and reduced substances in a medium whose formal composition is specified. A formal E therefore represents an empirical measure of the oxidizing power of a system that has a certain composition. A large difference between E° and the formal E of a given system indicates large complexing or activity effects. In practical cases, formal E 's may sometimes be more useful than E° values.

19D.2g. Other sign conventions. Some authors use the arrangement shown in Fig. 19.2, and identify a strongly reducing system with a high value of E . In this case the Nernst equation takes the form

$$E = E^\circ - \frac{0.0591}{n} \log \frac{Q_{ox}}{Q_{red}}$$

*The *formal concentration* (F) of a solute is the number of formula weights per liter of solution, without regard for the form in which the solute exists in solution. There is an advantage to the use of this term over the term "molarity." Thus it may not always be clear whether the term "5 M H_2SO_4 " represents the total H_2SO_4 concentration or just the un-ionized H_2SO_4 concentration. This ambiguity does not exist when formal concentrations are used.

Other plans also exist, the pros and cons of which have been discussed at great length. There is yet no universal agreement (B6).

Whenever an unfamiliar TSP is encountered, the student should orient himself with respect to (1) the arrangement in the table, by seeking the position of a substance of known properties, and (2) the associated Nernst equation, by ascertaining that an increase in Q_{ox} changes E in the direction of greater oxidizing strength. Oriented in this way, the student can calculate with E° values from any TSP, and is not implicitly dependent upon any particular plan, like that in Appendix IX.

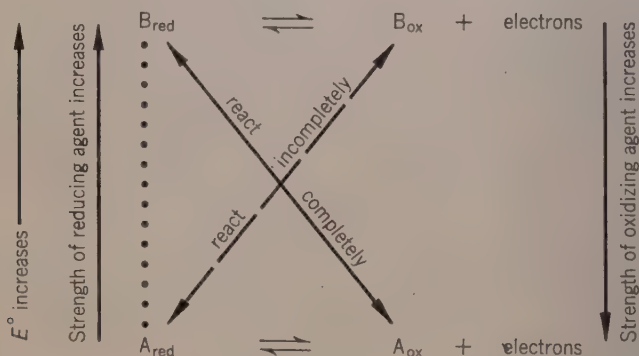
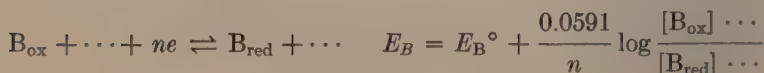


FIG. 19.2. Plan of the Table of Standard Potentials (with different sign convention)

19D.3. The Equilibrium Constant

Suppose that all the components of the following two half-reactions are mixed together in the same system.



If the E 's are different, reaction occurs, and the stronger oxidizer oxidizes the reduced form of the weaker oxidizer. For example, if $E_A > E_B$, then A_{ox} tends to oxidize B_{red} .



As the reaction proceeds toward equilibrium, A_{ox} and B_{red} are used up, and E_A and E_B approach each other. (E_A decreases as $[A_{\text{ox}}]$ decreases, and E_B increases as $[B_{\text{red}}]$ decreases.) The reaction continues until $E_A = E_B$, at which point there is no longer any tendency for A_{ox} to remove electrons from B_{red} , and equilibrium is reached. At equilibrium, $E_A = E_B$, and

$$E_A^\circ + \frac{0.0591}{n} \log \frac{[A_{\text{ox}}]}{[A_{\text{red}}]} = E_B^\circ + \frac{0.0591}{n} \log \frac{[B_{\text{ox}}]}{[B_{\text{red}}]}$$

$$E_A^\circ - E_B^\circ = \frac{0.0591}{n} \log \frac{[A_{\text{red}}][B_{\text{ox}}] \cdots}{[A_{\text{ox}}][B_{\text{red}}] \cdots}$$

$$10^{n(E_A^\circ - E_B^\circ)/0.0591} = \frac{[A_{\text{red}}][B_{\text{ox}}] \cdots}{[A_{\text{ox}}][B_{\text{red}}] \cdots} \quad (\text{At equilibrium}) \quad (19.9)$$

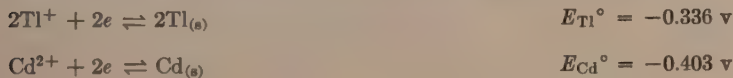
Equation 19.9 allows the equilibrium constant to be calculated from E° values in the TSP. From the equilibrium constant the composition of the system at equilibrium may be calculated when certain concentrations of the reducer and oxidizer are initially mixed together. In general, the reaction reaches equilibrium at some potential which is intermediate between the initial values of E_A and E_B , which in turn are dependent upon the initial composition of the system. The E at equilibrium may be calculated from the equilibrium composition of the system.

The foregoing derivation of Eq. 19.9 applies only to the special case for which the number (n) of electrons is the same for both half-reactions. Any other case may be made to conform to this case by multiplying each half-reaction throughout by an integer. Such multiplication does not change the E° for the half-reactions. The following examples should clarify the application of these principles.

It is inadvisable to memorize relationships like Eq. 19.9; these, like the Nernst equation, hold only for the particular sign convention used in their derivation. It is easier to derive these relationships in each application than it is to memorize them.

Example 1. A solution is 0.010 M in CdSO_4 and 0.0005 M in Tl_2SO_4 . When placed in contact with excess metallic Tl , what is the composition of the system at equilibrium?

The reaction may be considered to occur through the half-reactions



Initially, E_{Cd} is infinitely high, since there is no metallic Cd in the system. Hence reaction must occur to form some Cd metal.



At equilibrium, $E_{\text{Cd}} = E_{\text{Tl}}$, and

$$\begin{aligned} -0.403 + \frac{0.0591}{2} \log [\text{Cd}^{2+}] &= -0.336 + \frac{0.0591}{2} \log [\text{Tl}^+]^2 \\ \log \frac{[\text{Tl}^+]^2}{[\text{Cd}^{2+}]} &= \frac{2}{0.0591} (0.336 - 0.403) = -2.27 \\ \frac{[\text{Tl}^+]^2}{[\text{Cd}^{2+}]} &= 10^{-2.27} = 0.0054 \end{aligned}$$

With the equilibrium constant, it becomes possible to find the composition of the system at equilibrium. Let y be the moles of Cd metal precipitated per liter of solution. Then

$$\begin{array}{l} [\text{Cd}^{2+}] = 0.010 - y \\ \quad \quad \quad \uparrow \quad \quad \quad \uparrow \\ \quad \quad \quad \text{Initial concentration of } \text{Cd}^{2+}. \quad \text{Moles } \text{Cd}^{2+} \text{ removed per liter} \\ \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \text{by reduction to metal.} \\ \\ [\text{Tl}^+] = 0.0010 + 2y \\ \quad \quad \quad \uparrow \quad \quad \quad \uparrow \\ \quad \quad \quad \text{Initial concentration of } \text{Tl}^+. \quad \text{Moles } \text{Tl}^+ \text{ formed per liter.} \end{array}$$

These concentrations may be substituted into the equilibrium-constant expression, giving an equation which may be solved for y by successive approximations or trial and error.

$$\begin{aligned} \frac{(0.0010 + 2y)^2}{0.010 - y} &= 0.0054 \\ y, \text{ or } [\text{Cd}^{2+}] &= 0.00265 \text{ } M \end{aligned}$$

The equilibrium composition is

$$\begin{aligned} [\text{Cd}^{2+}] &= 0.010 - y = 0.010 - 0.00265 = 0.007 \text{ } M \\ [\text{Tl}^+] &= 0.0010 + 2y = 0.0010 + 2(0.00265) = 0.0063 \text{ } M \\ [\text{SO}_4^{2-}] &= 0.0105 \text{ } M \end{aligned}$$

Cd metal precipitated per liter of solution = $y = 0.0026$ mole.

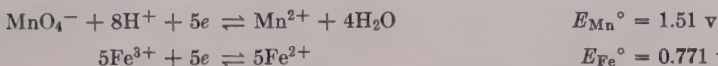
Tl metal also exists in the system, since it was added in excess.

The E at equilibrium may be found from either $[\text{Tl}^+]$ or $[\text{Cd}^{2+}]$, since E_{Tl} and E_{Cd} are identical.

$$E_{\text{Tl, equil.}} = -0.336 + 0.0591 \log (0.0063) = -0.466 \text{ v}$$

Example 2. A solution contains 0.001000 M KMnO_4 and 0.010 M H_2SO_4 . To this solution is added an exactly equivalent amount of FeSO_4 —that is, the solution is made 0.005000 M in FeSO_4 . Assuming that the FeSO_4 is added without changing the volume of the solution, and assuming that the H_2SO_4 is completely ionized, what are the composition and E of the solution at equilibrium?

Reaction may be considered to occur through the half-reactions



Initially there is no Fe^{3+} and no Mn^{2+} , so E_{Fe} is infinitely low and E_{Mn} is infinitely high. Reaction therefore occurs to form Fe^{3+} and Mn^{2+} .



At equilibrium, $E_{\text{Fe}} = E_{\text{Mn}}$, and

$$\begin{aligned}0.771 + \frac{0.0591}{5} \log \frac{[\text{Fe}^{3+}]^5}{[\text{Fe}^{2+}]^5} &= 1.51 + \frac{0.0591}{5} \log \frac{[\text{MnO}_4^-][\text{H}^+]^8}{[\text{Mn}^{2+}]} \\ \frac{[\text{Fe}^{3+}]^5[\text{Mn}^{2+}]}{[\text{Fe}^{2+}]^5[\text{MnO}_4^-][\text{H}^+]^8} &= 10^{5(1.51-0.771)/0.0591} = 4 \times 10^{62}\end{aligned}$$

From the value of the equilibrium constant, the equilibrium composition of the system may be found. Let $[\text{MnO}_4^-]$ at equilibrium be y . The large magnitude of the equilibrium constant indicates that the reaction between Fe^{2+} and MnO_4^- is practically quantitative, and that y is negligible compared to 0.001000 M . From the stoichiometry of the reaction,

$$\begin{array}{l}[\text{Mn}^{2+}] = 0.001000 - y \cong 0.001000 \text{ } M \\ [\text{Fe}^{3+}] = (0.001000 - y)5 \cong 0.005000 \text{ } M \\ [\text{Fe}^{2+}] = 0.005000 - (0.001000 - y)5 = 5y \text{ } M \\ \quad \quad \quad \uparrow \quad \quad \quad \uparrow \\ \quad \quad \quad \text{Initial Fe}^{2+} \text{ concentration.} \quad \text{Fe}^{2+} \text{ used in reaction.} \\ [\text{H}^+] = 0.020 - 8(0.001000 - y) \cong 0.012 \text{ } M \\ \quad \quad \quad \uparrow \quad \quad \quad \uparrow \\ \quad \quad \quad \text{Initial H}^+ \text{ from H}_2\text{SO}_4. \quad \text{H}^+ \text{ used in reaction.}\end{array}$$

Substituting these concentrations into the equilibrium-constant expression gives an equation which can be solved for y .

$$\begin{aligned}\frac{(0.005000)^5(0.001000)}{(5y)^5(y)(0.012)^8} &= 4 \times 10^{62} \\ y, \text{ or } [\text{MnO}_4^-] &= 1.3 \times 10^{-11} \text{ } M\end{aligned}$$

The small value of y justifies the assumption that y is negligible compared to 0.001 M .

With y known, it is left as an exercise for the student to specify the equilibrium composition of the system, and to calculate the equilibrium E as 1.237 v.

19E. THE ELECTROCHEMICAL CELL

All electrochemical methods of analysis are based on the measurement of voltages or currents in electrochemical (i.e., voltaic) cells. The workings of such cells are described in this section, together with the measurement and use of cell voltage for analytical purposes.

19E.1. Description

In Sec. 19D.3 the impression is given that a reducer (such as Zn metal) and an oxidizer (such as AgNO_3) must be in direct contact with each other before the redox reaction can occur. While this is the most direct way to bring about the reaction, such direct contact is unnecessary. It is only necessary that electrons from the reducer be able to reach the oxidizer. Thus reaction may occur in a device such as that shown in Fig. 19.3C, which is an electrochemical cell.

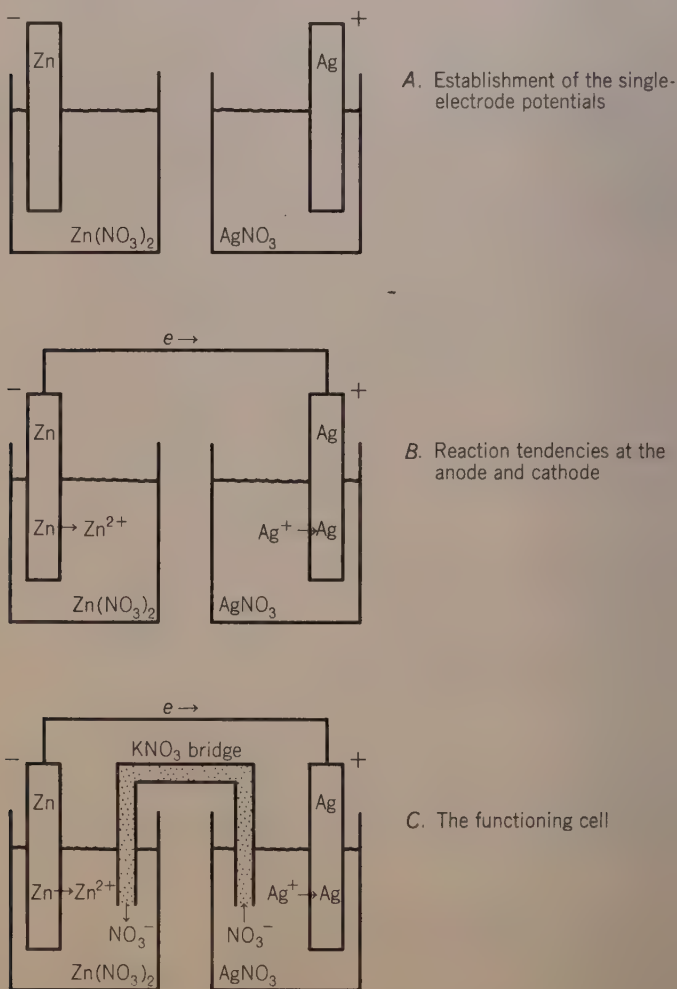


FIG. 19.3. The Electrochemical Cell

When a Zn strip is immersed in a 1 *M* Zn(NO₃)₂ solution, a voltage is set up between the strip and the solution. The magnitude of this voltage is *E*.*

$$E_{\text{Zn}} = E_{\text{Zn}}^{\circ} + \frac{0.0591}{2} \log [\text{Zn}^{2+}] = -0.763 \text{ v}$$

In similar fashion, the voltage of an Ag strip immersed in 1 *M* AgNO₃ is +0.799 v with respect to the solution. This situation is represented in Fig. 19.3A. The Zn electrode is more negative than the Ag electrode, and when the two strips are connected with a wire, electrons flow from the Zn to the Ag. This electron transfer raises the Zn electrode voltage, and lowers the Ag electrode voltage. Consequently, some Zn metal becomes oxidized at the Zn electrode, and some Ag⁺ is reduced at the Ag electrode (Fig. 19.3B).

The process stops almost immediately, since the solution surrounding the Zn electrode becomes positively charged, while the solution around the Ag electrode becomes negatively charged. If appreciable quantities of Zn are to be put into solution, the solution must be kept electrically neutral (p. 187). This can be accomplished only by the passage of negative ions into the left-hand compartment. In similar manner, negative ions must be transported out of the right compartment if discharge of Ag⁺ is to continue. Only when there is established a path along which ions may migrate between the two compartments may appreciable reaction occur. Such a path is furnished by a *bridge*, which is a porous tube filled with an inert electrolyte, such as KNO₃. Such a working cell is shown in Fig. 19.3C.† In this cell appreciable amounts of oxidation and reduction occur, and appreciable amounts of work may be done by electrons flowing in the external circuit. Such electrical

*The absolute magnitude of the voltage between the electrode and solution is unknown, and cannot be measured. Only differences in voltage between two electrodes can be measured. The *E* is a relative or differential voltage, which is the difference between the voltage of an electrode and the voltage of a standard hydrogen electrode.

$$\left(E \text{ of the} \right)_{\text{electrode}} = \left(\text{true voltage of} \right)_{\text{the electrode}} - \left(\text{true voltage of the} \right)_{\text{standard hydrogen electrode}}$$

It is no hindrance that the true voltages are unknown, for only differences in voltages between two electrodes are ever used in computations. The difference between two *E*'s is the same as the difference between their true voltages.

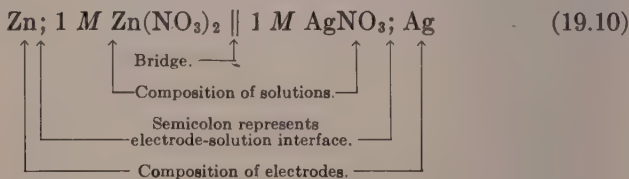
† The ion current is not furnished by the nitrate alone, as shown in the figure. Neutralization of compartmental charge may also be achieved if positive ions flow from the left to the right compartment. Actually, both processes occur simultaneously. The net effect is that KNO₃ builds up around the Ag electrode, while Zn(NO₃)₂ builds up around the Zn electrode as the reaction proceeds.

work could not be performed if the AgNO_3 were allowed to contact the Zn metal directly.

The metallic electrode need not be the reduced form of the reagent, as in the example above. Inert electrodes are often used. For example, a Pt electrode immersed in a solution containing Fe(II) and Fe(III) acquires a charge with respect to the solution. Also, if electrons are supplied to the Pt electrode, reduction of Fe(III) to Fe(II) can occur at the surface. If electrons are removed, oxidation of Fe(II) to Fe(III) can occur.

Regardless of the polarity, that electrode at which oxidation takes place is called the *anode*, while that electrode at which reduction takes place is called the *cathode*. In the cell of Fig. 19.3, the positive Ag electrode is the cathode, and the negative Zn electrode is the anode.

Compositions of electrochemical cells are conventionally expressed in a shorthand way (D1). The following example describes the cell of Fig. 19.3.



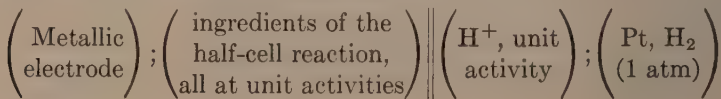
The following cell is composed of a *hydrogen electrode*, which is a platinum electrode immersed in a 0.1 *M* HCl solution saturated with hydrogen gas at 0.1 atm. The other electrode is copper immersed in 0.05 *M* CuCl_2 . The composition of the bridge is not specified.



19E.2. Voltage and Polarity

The voltage generated by a cell is the difference between the E 's of the two systems constituting the cell. That electrode with the higher E is positive, and reduction occurs there. The following examples illustrate this reasoning.

By measuring cell voltages, E values of different kinds of single-electrode systems may all be found relative to each other. The E° values of Appendix IX are such relative values, with the E° for the standard hydrogen half-cell taken as zero. Thus an E° value in Appendix IX represents the voltage of a cell composed of the single electrode in question and the standard hydrogen electrode.



Example 1. What are the voltage and polarity of the cell of Fig. 19.3, if the concentration of $\text{Zn}(\text{NO}_3)_2$ is 0.050 *M* and the concentration of AgNO_3 is 0.090 *M*?

$$E_{\text{Zn}} = E_{\text{Zn}}^\circ + \frac{0.0591}{2} \log [\text{Zn}^{2+}] = -0.763 + \frac{0.0591}{2} \log 0.050 = -0.801 \text{ v}$$

$$E_{\text{Ag}} = E_{\text{Ag}}^\circ + 0.0591 \log [\text{Ag}^+] = 0.799 + 0.0591 \log 0.090 = 0.737 \text{ v}$$

The Ag electrode is positive, since its *E* is the more positive, and reduction of Ag^+ occurs there.

The cell voltage is reckoned as 1.538 v, as follows:

$$\begin{array}{ccc} E_{\text{Zn}} & & E_{\text{H}}^\circ & & E_{\text{Ag}} \\ | & & | & & | \\ -0.801 \text{ v} & & 0 & & 0.737 \text{ v} \\ \hline & \text{Difference} = 0.737 - (-0.801) = 1.538 \text{ v} & & & \end{array}$$

Example 2. The following cell has a voltage of 0.484 v, the calomel electrode being negative. Calculate E° for the half-reaction $\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$.

Pt; 0.010 *M* Fe^{2+} , 0.0020 *M* Fe^{3+} || saturated calomel electrode

Since the Fe^{3+} - Fe^{2+} electrode is positive, it must have a higher *E* than the calomel electrode. Since the calomel electrode is 0.246 v more positive than the standard hydrogen electrode, the *E* of the Fe^{3+} - Fe^{2+} electrode with respect to the standard hydrogen electrode must be $0.246 + 0.484 = 0.730$ v.

$$E_{\text{Fe}}^\circ = E_{\text{Fe}} - 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} = 0.730 - 0.0591 \log \frac{0.0020}{0.010} = 0.771 \text{ v}$$

19E.3. Measurement of Single-Electrode Potentials

To measure the *E* of a system, that system is combined into an electrochemical cell with another single electrode of known *E*. Measurement of the voltage of the cell then allows calculation of the *E* of the electrode in question, as shown in the preceding example.

The *standard hydrogen electrode* (Fig. 19.4) is a reference electrode that is occasionally used for the measurement of *E* values of other electrodes. The standard hydrogen electrode has an *E* of zero, but it is not as convenient to use as other reference electrodes. A more practical reference electrode is the *calomel electrode*, which is stable, easy to prepare, and has an accurately known *E*. Most forms of this electrode have the bridge built right into the electrode itself, as shown in Fig. 19.5.

The measurement of cell voltages is not so simple that it may be done with an ordinary voltmeter, even though the voltages are of the order of several volts. To obtain a correct value the voltage must be measured without allowing any appreciable current to flow. If appreciable current flows during measurement, the electrodes become *polarized*—that is, the solution immediately surrounding the electrode becomes depleted with respect to the oxidizable (or reducible) substance,

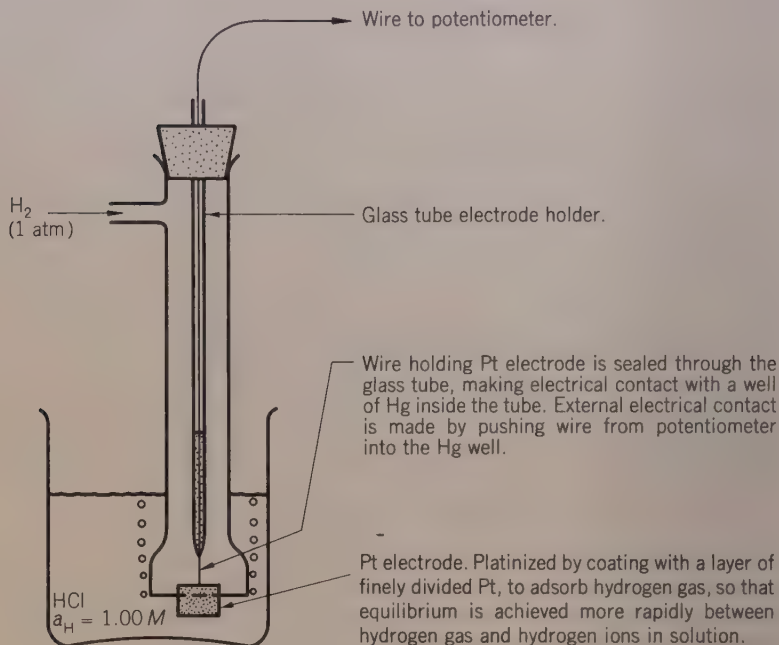
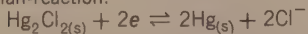


FIG. 19.4. A Standard Hydrogen Electrode

because it is removed by oxidation (or reduction) faster than it can be replaced by diffusion from the bulk of the solution. When polarization occurs, the lowered concentration of oxidizable (or reducible) material at the electrode may cause error in the voltage measurement.

Bridge. Usually obstructed, to prevent siphoning. End of bridge dips into system whose E is to be measured.

*Half-reaction:



For the normal calomel electrode, KCl is 1 M, and $E = 0.282$ v.

For the saturated calomel electrode, KCl is saturated, and $E = 0.246$ v.

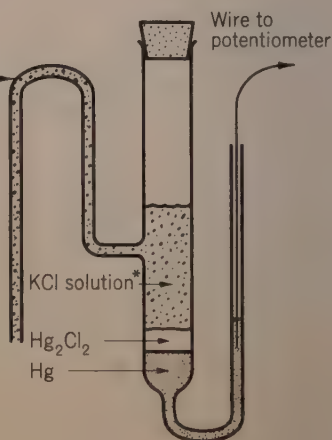


FIG. 19.5. A Calomel Electrode

One of the simplest instruments for measuring a voltage without drawing current is the *potentiometer*. The heart of the potentiometer is indicated within the dotted lines of Fig. 19.6. The unknown voltage is connected across *a* and *b*. Current from an outside voltage source flows through the highly uniform potentiometric resistance, which causes a uniform voltage drop throughout its length. In practice, the position of the tap *t* is adjusted so that no current flows through *G*. At this point, the voltage drop (measurable, since it is proportional to the length of *xt*) across the portion *xt* of the potentiometer must equal the voltage of the unknown source. Since *G* reads zero, no current is drawn from the unknown source. The mode of operating a simple potentiometer for measuring an unknown voltage is outlined in Fig. 19.6. The simple potentiometer of this figure is inadequate for measuring the voltage of a source with high resistance; for such a purpose, a *vacuum-tube voltmeter* must be used. A vacuum-tube voltmeter measures a voltage without balancing and with negligible current drain, but description of this instrument is beyond the scope of this book.

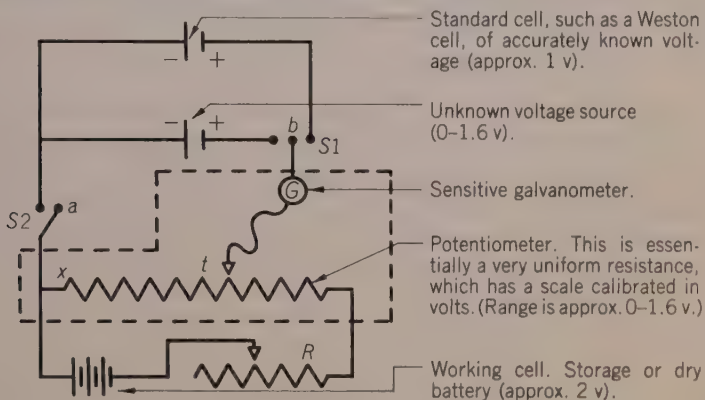


FIG. 19.6. Schematic Diagram of a Potentiometer—Procedure for measuring an unknown voltage: (1) Calibrate the potentiometer scale. Close *S1* to put standard cell across potentiometer. Set potentiometer dial to read exactly the voltage of the standard cell. Then adjust *R* so that there is no deflection of *G* when *S2* is momentarily closed. This operation adjusts the current from the working battery so that the voltage drop across the potentiometer agrees with the voltage reading on the potentiometer scale. Because the voltage of the working battery may slowly change as current is drawn, this calibration must be made frequently. (2) Measure the unknown voltage. Close *S1* to put the unknown voltage across the potentiometer. Adjust potentiometer dial so that there is no deflection of *G* when *S2* is momentarily closed. When this balance is made, the voltage across the potentiometer (readable from the scale) is the same as the unknown voltage. Voltages may be measured very accurately in this way.

19E.4. Amount of Electricity Obtainable from a Cell. Faraday's Law

The unit quantity of electricity is the *coulomb* (i.e., ampere-second), which is defined as the quantity of electricity passing a given point in a circuit when a current of 1 ampere flows for 1 second.

$$\text{Coulombs} = \text{amperes} \times \text{seconds} \quad (19.11)$$

In order to transform one equivalent of an oxidizing or reducing agent, a certain quantity (one equivalent) of electrons is required. This quantity has been carefully measured in terms of coulombs, and is 96,496 coulombs per equivalent. This unit of electricity is called the *Faraday*. Thus reduction of one equivalent of an oxidizing agent requires 96,496 coulombs, or a current of 1 ampere flowing for 96,496 seconds.

The total quantity of electricity that may be delivered by a cell is calculable if the initial and equilibrium compositions are known. There need be computed only the equivalents of reducible or oxidizable material transformed in passing from the initial to the final state, and from this may be found the coulombs of electricity obtainable.

$$\text{Coulombs} = \text{equivalents transformed} \times 96,496 \quad (19.12)$$

A distinction must be made between the *amount* of electricity which flows in a circuit and the electrical energy or *work* performed by that amount of electricity. The work is dependent not only on the quantity of electricity that flows, but also upon the potential through which the quantity falls. If it is possible to carry out the cell reaction at a constant cell voltage, V , then the maximum electrical work obtainable in watt-seconds (or joules) is

$$\text{Work} = \text{volts} \times \text{amperes} \times \text{seconds (in watt-seconds, or joules)} \quad (19.13)$$

$$\text{Work} = V \times 96,496 \text{ watt-seconds per equivalent transformed} \quad (19.14)$$

In practice, however, unless the cell is infinitely large, V falls as current is drained, and the practical electrical work obtained is less than the maximum shown above. The electrical work is dissipated as heat in the resistance of the cell circuit. The work dissipated in the internal resistance (i.e., the resistance of the cell itself) is wasted; the useful work is that dissipated in the resistance of the external circuit.

A more widely used unit of work is the *calorie*, which is the energy required to heat 1 g of water from 14.5 to 15.5°C. One calorie is equivalent to 4.184 watt-seconds, or joules.

Example 1. A constant current source delivers 0.0765 amps through a metal plating bath. How long must the apparatus run to plate 0.129 g of Ag?

$$\frac{0.129}{107.870} \left| \begin{array}{c} \times 96,496 \\ \text{—eq Ag} \end{array} \right| \times \frac{1}{0.0765} \left| \begin{array}{c} \times \\ \text{—coulombs required} \end{array} \right| = 1.51 \times 10^3 \text{ sec}$$

Example 2. Per mole of Ag^+ reduced, what is the maximum amount of electrical work obtainable from an infinitely large cell of the type in Ex. 1, page 417?

Per mole of Ag^+ reduced, the work is $1.538 \times 96,496 = 1.484 \times 10^5$ watt-sec, or joules. This is $1.484 \times 10^5 / 4.184 = 3.547 \times 10^4$ cal.

The cell must be infinitely large to obtain this amount of work, so that the removal of a mole of Ag^+ from the right compartment and the introduction of a half-mole of Zn^{2+} into the left compartment do not appreciably change the composition. Then the voltage remains practically constant at 1.538 v.

Example 3. Suppose that the cell of Ex. 1, page 417, contains large Zn and Ag electrodes, but that there are only 2.00 l of 0.050 M $\text{Zn}(\text{NO}_3)_2$ in the left compartment and 1.50 l of 0.090 M AgNO_3 in the right compartment. What is the quantity of electricity obtainable if this cell is allowed to run to equilibrium?

It may be seen without calculation that virtually all the silver is reduced and that there is produced $1.50 \times 0.090 \times 96,496 = 1.30 \times 10^4$ coulombs.

This quantity of electricity is not all liberated at the initial voltage of 1.538 v, for the voltage drops as Ag^+ is depleted and as Zn^{2+} builds up, approaching zero at equilibrium. The amount of work is calculated in the supplementary problems (see Prob. S1, p. 817).

19E.5. Calculation of Equilibrium Constants

Fundamentally, the E of an electrode system is a function (and therefore a measure) of the concentrations of the solute species in that system. From the E of a system containing a precipitable solute species and a known concentration of a precipitating agent, the concentrations of the solute species within that system may be found. From these concentrations the solubility product for the precipitation reaction may be calculated. Such a calculation is shown in the following example.

Example 1. Suppose that a metal (M) forms an insoluble chloride, MCl_2 . From the following data, calculate the solubility product of MCl_2 .



$$E^\circ = 0.053 \text{ v}$$



The voltage of the cell is 0.596 v; the M electrode is negative.

The E of the M electrode may be calculated. Since the M electrode is negative, oxidation occurs at this electrode, and its E must be below that of the calomel electrode. Hence, with respect to the standard hydrogen electrode, the E of the M electrode is $-0.596 + 0.246 = -0.350$ v. This reasoning may be clarified with the accompanying diagram.

From the above concentrations, K_a may be calculated.

$$K_a = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} = \frac{(0.00020)(0.00020)}{0.0098} = 4.1 \times 10^{-6}$$

Equilibrium constants for complex-ion formation may be found in a similar manner. A cell is devised in which the E of one electrode is sensitive to the concentration of the complexable solute species. By measuring the E of this electrode in the presence of a known concentration of the complexer, the equilibrium constant for the complexing reaction may be calculated, as illustrated in the following example.

Example 3. The metal ion, B^+ , forms a chloro complex according to the reaction



E° for the $\text{B}^+ - \text{B}_{(s)}$ half-reaction is 0.550 v. Calculate K if the voltage of the following cell is 0.052 v and the B electrode is positive. Neglect activity effects.

B; 0.00100 M BNO_3 , 0.0050 M KCl || saturated calomel electrode

The E of the B electrode may be calculated. Since the B electrode is positive, its E must lie above that of the normal calomel electrode. Hence the E of the B electrode with respect to the standard hydrogen electrode is $0.052 + 0.246$, or 0.298 v.

From E , $[\text{B}^+]$ may be calculated.

$$0.298 = 0.550 + 0.0591 \log [\text{B}^+]$$

$$[\text{B}^+] = \text{antilog} \left(-\frac{0.252}{0.0591} \right) = 5.5 \times 10^{-5} M$$

The concentrations of the other ion species necessary for an evaluation of K may now be computed.

From a consideration of the material balance on B^+ ,

$$[\text{BCl}_2^-] = 0.00100 - 0.000055 = 0.00094 M$$

$\begin{array}{ccc} \uparrow & & \uparrow \\ \text{Total B}^+ & & \text{Free B}^+ \end{array}$

From a consideration of the material balance on Cl^- ,

$$[\text{Cl}^-] = 0.0050 - 2(0.00094) = 0.0031 M$$

$\begin{array}{ccc} \uparrow & & \uparrow \\ \text{Total Cl}^- & & \text{Cl}^- \text{ complexed as } \text{BCl}_2^- \end{array}$

$$K = \frac{[\text{BCl}_2^-]}{[\text{B}^+][\text{Cl}^-]^2} = \frac{(0.00094)}{(5.5 \times 10^{-5})(0.0031)^2} = 1.8 \times 10^6$$

19E.6. Accuracy of Calculations Involving E° Values

What is said about the accuracy of calculations involving solubility-product values (p. 172) applies to calculations made from E° values. Correction for activity effects is given in the Supplement (p. 808).

In addition, there are sources of error involved in the experimental determination of E values that are beyond the scope of this book. The voltage of an electrochemical cell may be contributed to not only by the E 's of the two electrode systems, but also by *junction potentials* between media of differing composition, *polarization* effects, and *overvoltage* effects. It is difficult to obtain a good estimate of an E because it is difficult to eliminate or correct for these other effects.

19F. ADDITIONAL CONSIDERATIONS IN USING THE TABLE OF STANDARD POTENTIALS

In Sec. 19D (p. 404) the extent of a redox reaction is predicted from equilibrium considerations alone, according to the difference in E 's of the component half-reactions. However, other considerations beside the equilibrium state may profoundly affect the extent and even the course of a redox reaction. Among such considerations are: (1) complexers, (2) reaction rate, (3) simultaneous reactions, (4) consecutive reactions, and (5) irreversible reactions. These are discussed qualitatively in the following sections. Because of their complexity, the theory of these effects is not so well and quantitatively developed as equilibrium theory.

Complexers. The TSP lists oxidizing and reducing agents in order of their strengths when all species involved in the half-reactions are at standard states. If one or more species are at other than standard states, the E of the couple is different from E° . Actually, the E (i.e., oxidizing strength) of a given half-reaction may be varied greatly with complexers or precipitants. Examples are given in Sec. 19D.2e (p. 408).

In particular, H^+ is involved in many half-reactions, and the pH may therefore markedly affect the E of a system. For example, E° for the $Cr(VI)$ - $Cr(III)$ half-reaction is 1.33 v in acid solution, and only -0.13 v in basic solution. The same is true of ozone, as shown in Ex. 2, page 408.

Control of the pH is often used to control the extent of a redox reaction, either to bring it about more easily, or to prevent its occurrence. The iodimetric determination of As is an excellent example (p. 461).

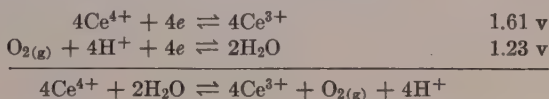
Reaction rate. It is pointed out in Sec. 4D (p. 30) that many reactions have high tendencies but low rates—that is, they would go very completely if enough time were allowed, but their rates are so low that equilibrium is not attained within practical time limits. The TSP tells nothing about the rates at which substances react. Although there are some generalizations, rate theory is not so well developed that it may be summarized in as comprehensive a form as the TSP.

In general, if information is desired on the rate of a specific reaction, it is best obtained from the literature or the laboratory.

Any conclusions drawn from the TSP are therefore definite only in a negative sense. That is, if a reaction has a low tendency and the equilibrium lies far to the left, then this reaction will definitely not go appreciably to the right. But if the tendency is high and the equilibrium is far to the right, it is still necessary to ascertain that the rate is appreciable before the reaction may be said actually to occur. As a corollary to these statements, there is no point in looking for a catalyst to bring about a desired reaction unless the equilibrium is favorable.

The following two examples deal with reactions having high tendencies but low rates. It is not feasible to omit from the TSP the half-reactions involved in such slow reactions, for these very same half-reactions are involved in other reactions that have appreciable rates.

Example 1. According to the TSP, Ce(IV) should oxidize water quite completely, and should therefore be unstable according to the reaction



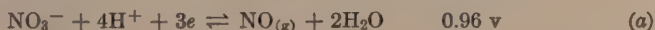
However, $\text{Ce}(\text{SO}_4)_2$ in aqueous 1 *M* H_2SO_4 is a very good oxidizing agent, and is so stable that it may be used as a standard solution for titrations. The rate of the above reaction is nil.

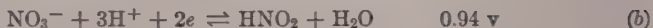
Example 2. The oxidation of V(IV) to V(V) by dichromate (and even permanganate) is very complete according to the TSP, but the rate is low at room temperature. For analytical purposes, the oxidation of V is performed at elevated temperature, to hasten the reaction.

A brief discussion of the mechanism of redox reactions is given in the Supplement (p. 809), together with examples of analytical interest.

Simultaneous reactions. It often happens that a particular oxidizing or reducing agent may be changed to more than one other oxidation state. If the *E*'s of the different processes are roughly the same, then the reaction may proceed simultaneously according to several individual equations. The relative extent to which each of the possible individual processes occurs is often more dependent upon their relative rates than upon their individual equilibrium constants.

Example 3. A more complete table of standard potentials (L6) shows the following half-reactions for nitrate in acid solution.





Therefore, if nitrate is reduced in acid solution, three over-all equations are required to describe the course of the reduction: one in which nitrate is reduced to NO, another in which nitrate is reduced to HNO₂, and a third in which nitrate is reduced to N₂O₄. The extent to which each of these three individual reactions occurs is not determined solely by the equilibrium constants of the three reactions, but rather by the relative rates at which the three reactions occur and by the proportions of oxidizer and reducer. Generally, it is not only complicated but also pointless to try to calculate the relative extents of simultaneous reactions from equilibrium considerations alone.

Consecutive reactions. After it is decided that a certain reaction (or reactions) may occur according to the TSP, it is necessary to look further at the system, to ascertain that the products of the reaction do not react further with other components of the system. There is always the possibility of further reaction between a product and (1) an excess of a reagent, (2) water, or (3) some component of the air, if the system is accessible to air. Such investigation was made in Ex. 1, page 399. The example below illustrates further application of these principles.

Example 4. The following reactions (16) describe the redox behavior of the products (NO, HNO₂, and N₂O₄) of reactions *a* to *c* in Ex. 3 above.



In case there is excess reducing agent, it may be seen that any N₂O₄ or HNO₂ formed by reduction of nitrate (Eqs. *b*, *c*) does not survive, but is reduced further by excess reductant according to Eqs. *d* to *g*. NO and N₂O are the principal products if there is excess reducing agent. (Reaction rates are ignored in this example.)

Irreversible reactions. Some of the half-reactions of Appendix IX are not reversible, and cannot be used in equilibrium calculations. An example is the half-reaction



It is meaningless to calculate an equilibrium constant for the oxidation of H₂C₂O₄ by an oxidizer, because once oxidized, the CO₂ and H⁺ do not recombine to form H₂C₂O₄. Most other organic substances (formaldehyde, etc.) behave similarly. However, *E*[°] values for some irre-

versible reactions may be measured and calculated indirectly, and are included in the TSP because they are useful in other applications, especially in explaining equilibria that are important in biochemical processes.

QUESTIONS

Sections 19A, B

1. Give the oxidation numbers of the elements in the following ions or molecules: $\text{S}_2\text{O}_3^{2-}$, $\text{S}_4\text{O}_6^{2-}$, PO_3^{2-} , $\text{Na}_2\text{C}_2\text{O}_4$, Na_2CO_3 , PO_2^{2-} , VO^{2+} , MnO_4^- , Sb_2O_3 , N_2O_4 , VO_2^+ , IrCl_6^- , HClO_3 , NaOCl , $(\text{UO}_2)\text{SO}_4$, PO_4^{3-} , Fe_2O_3 , AlO_2^- , $\text{Cr}_2\text{O}_7^{2-}$, $\text{Na}_2\text{S}_2\text{O}_5$, KNO_3 , H_2SO_3 .

2. What is inadequate or incorrect about each of the following statements? (a) An oxidizing agent is an oxygen donor. (b) A substance which is low in the TSP is a strong reducer.

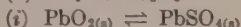
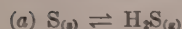
3. Why would nitrate and perchlorate not react with each other?

4. Find in the TSP substances that may act as either oxidizers or reducers.

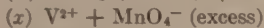
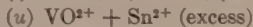
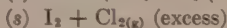
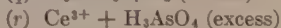
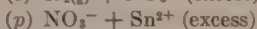
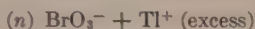
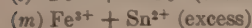
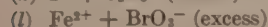
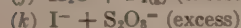
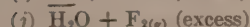
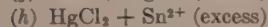
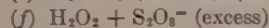
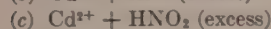
5. Which of the following reducers would be most effective in reducing Fe^{3+} to Fe^{2+} : metallic Zn, metallic Ag, SnCl_2 , or KI?

6. When Fe metal is dissolved in acid solution, much of it is oxidized to Fe^{3+} . In such a solution, it is desired to reduce the Fe^{3+} quantitatively to Fe^{2+} , so that the latter may be determined by titration with standard KMnO_4 . From information in the TSP, describe how such a reduction may be carried out, with provision for eliminating any remaining excess of reductant that might cause error by reacting with the KMnO_4 .

7. Balance each of the following half-reactions in acid medium.



8. Neglecting reaction rates, write balanced chemical equations for each of the following redox reactions in acid solution, including those reactions that occur only to a very slight extent. Indicate on which side the equilibrium predominantly lies. For cases in which no reaction occurs, write "no reaction."



9. Complete and balance the equations for the following reactions in acid solution.

- (a) $\text{Zn} + \text{NO}_3^- \rightleftharpoons \text{Zn}^{2+} + \text{NH}_4^+$ (c) $\text{MnO}_4^- + \text{S}_4\text{O}_6^{2-} \rightleftharpoons \text{Mn}^{2+} + \text{SO}_4^{2-}$
 (b) $\text{O}_{2(g)} + \text{H}_2\text{S}_{(g)} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_2\text{O}$ (d) $\text{Cl}_{2(g)} + \text{Au} \rightleftharpoons \text{HAuCl}_4$

10. Complete and balance the equations for the following reactions in basic solution.

- (a) $\text{Zn} + \text{H}_2\text{O} \rightleftharpoons \text{ZnO}_2^{2-} + \text{H}_{2(g)}$ (d) $\text{Mg} + \text{NO}_3^- \rightleftharpoons \text{Mg(OH)}_2 + \text{NH}_3$
 (b) $\text{Bi(OH)}_3 + \text{SnO}_2^{2-} \rightleftharpoons \text{Bi} + \text{SnO}_3^{2-}$ (e) $\text{S}^{2-} + \text{I}_2 \rightleftharpoons \text{SO}_4^{2-} + \text{I}^-$
 (c) $\text{Fe(OH)}_2 + \text{O}_{2(g)} \rightleftharpoons \text{Fe(OH)}_3$

11. Write balanced equations for each of the following disproportionations in acid solution, and indicate on which side each equilibrium lies predominantly:
 (a) Hg_2^{2+} , (b) Sn^{2+} , (c) V^{3+} , (d) Cr^{3+} , (e) I_2 , (f) MnO_2 .

12. Describe the reaction that occurs, if any, in a solution made up to contain equimolar amounts of Hg^{2+} , Hg_2^{2+} , Fe^{2+} , and Fe^{3+} .

Section 19C

1. Compare the relative advantages and disadvantages of each of the following ways of expressing standard solution concentrations in redox calculations: molarity, normality, and titer.

2. To Table 19.1 (p. 402), add three other oxidizing or reducing agents, each of which shows more than one equivalent weight.

3. What is meant by the equivalent weight of iodine?

4. If a K_2CrO_4 solution is 0.1 *N* when used as an oxidizing agent, how is its concentration best expressed when used as a precipitant for Pb^{2+} in acid solution, to form PbCrO_4 ?

5. Distinguish between redox normality and acid-base normality.

6. Give examples of a direct and an indirect redox method of determination.

Section 19D

1. There are mixed into the same solution an oxidizing agent (A_{ox}) and a reducing agent (B_{red}), which tend to react quite completely with each other. From the instant of mixing until equilibrium is attained, describe the changes in the E 's of the two half-reactions. Is it correct to say that the solution has an E before equilibrium is attained?

2. What is inadequate or incorrect about the following statements? (a) Cerate is a stronger oxidant than bromate. (b) An element is more strongly reducing, the lower its oxidation state.

3. From the relative positions of pertinent half-reactions in the TSP:

(a) What are the relative stabilities of the ferrocyanide and ferricyanide complexes?

(b) What are the relative solubilities of AgCl , AgBr , and AgI ?

(c) What are the relative solubilities of Fe(OH)_2 and Fe(OH)_3 ?

4. How does the reducing strength of H_3AsO_3 depend upon acidity? How does the oxidizing strength of I_2 depend upon acidity? If it were desired to make the reaction between I_2 and H_3AsO_3 occur completely, what should be the acidity of the medium?

5. H_2O_2 may act as either an oxidizer or a reducer. What conditions of acidity favor its behavior as an oxidizer? As a reducer?

6. What conclusions may be drawn from the relative positions of the Hg^{2+} - Hg_2^{2+} and HgCl_2 - Hg_2Cl_2 half-reactions in the TSP?

7. Is it possible to maintain roughly equal concentrations of Ag(I) and Fe(II) together in the same solution without formation of Fe(III) and Ag metal ? Explain how introduction of excess cyanide would prevent reduction of Ag(I) by Fe(II) .

8. In which direction does each reaction of Prob. 10, Sec. 19D (p. 434), proceed, if all reagents and products are mixed at their standard states?

9. The use of concepts and properties whose absolute values are unmeasurable is not at all unusual in science. Name and discuss such properties, other than the single-electrode potential.

10. Theoretically, when the pure reduced form of a reagent is put into pure water, the E of the system is infinitely low. The pure oxidized form of a reagent should likewise give a very high E . Explain why such very low or high values are not attained in real solutions.

11. What would happen if HCl instead of HNO_3 were used as the source of H^+ in Ex. 2, page 407?

12. From Appendix IX, find a system for which the formal E is considerably different from E° . Speculate on the reasons for the difference.

13. Why does E° for the Hg_2Cl_2 - Hg half-reaction differ from E for the normal calomel half-cell?

14. A TSP other than that in Appendix IX gives:



Locate the positions and give the E° 's of the following half-reactions: H_2 - H^+ ; Cr^{3+} - $\text{Cr}_2\text{O}_7^{2-}$; Sn^{2+} - Sn^{4+} .

Section 19E

1. In Fig. 19.3C (p. 414), why not dispense with the bridge, putting the Ag and Zn electrodes into a single solution containing AgNO_3 and $\text{Zn(NO}_3)_2$?

2. Diagram the following cells. Give the polarity of each electrode and the reaction occurring at each electrode.

(a) $\text{Pt}, \text{H}_2 (0.2 \text{ atm}); 0.001 \text{ M HCl} \parallel 0.01 \text{ M NaCl}, \text{Hg}_2\text{Cl}_{2(s)}; \text{Hg}$

(b) $\text{Ag}; \text{AgCl}_{(s)}, 0.003 \text{ M HCl} \parallel 0.010 \text{ M FeCl}_2, 0.010 \text{ M FeCl}_3; \text{Pt}$

(c) $\text{Pt}; 0.040 \text{ M Ce(SO}_4)_2, 0.0010 \text{ M Ce}_2(\text{SO}_4)_3 \parallel 0.010 \text{ M Ce(SO}_4)_2, 0.020 \text{ M Ce}_2(\text{SO}_4)_3; \text{Pt}$

(d) $\text{Pt}; 0.020 \text{ M UO}_2(\text{SO}_4)_2, 0.010 \text{ M U(SO}_4)_2, 0.10 \text{ M H}_2\text{SO}_4 \parallel 0.020 \text{ M CuSO}_4; \text{Cu}$

3. Explain why the polarity of any real hydrogen electrode is always negative with respect to the normal calomel electrode.

4. In each of the following cells, which electrode is positive? In each case, explain how the polarity may be reversed by changing the concentration of only one solute species.

(a) $\text{Zn}; 0.05 \text{ M ZnCl}_2 \parallel 0.01 \text{ M ZnCl}_2; \text{Zn}$

(b) $\text{Pt}; 0.030 \text{ M FeCl}_2, 0.010 \text{ M FeCl}_3 \parallel 0.010 \text{ M FeCl}_2, 0.020 \text{ M FeCl}_3; \text{Pt}$

(c) $\text{Pt}, \text{H}_2 (0.01 \text{ atm}); 0.06 \text{ M HCl} \parallel 0.01 \text{ M HCl}; \text{H}_2 (1 \text{ atm}), \text{Pt}$

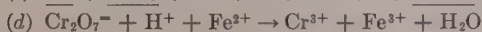
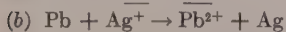
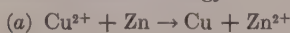
(d) $\text{Ag}; \text{AgCl}_{(s)}, 0.010 \text{ M NaCl} \parallel 0.020 \text{ M AgNO}_3; \text{Ag}$

(e) $\text{Pt}, \text{O}_2 (1 \text{ atm}); 0.020 \text{ M H}_2\text{SO}_4 \parallel 0.020 \text{ M H}_2\text{SO}_4; \text{H}_2 (1 \text{ atm}), \text{Pt}$

5. How would the E° values of Appendix IX be changed if the normal calomel electrode were used as the standard reference electrode (i.e., taken to be 0.000 v)?

6. In the cell of Ques. 4a, what would be the effect on the polarity if excess NaOH were added to the right-hand compartment?

7. Describe electrochemical cells in which the following reactions could be used to produce electrical energy.



8. Consider carefully the electrode processes which occur when current is drawn from the cell of Ques. 4a and explain what effect polarization has on the cell voltage.

9. What happens to the voltage and composition of the cell of Ques. 4a after appreciable amounts of current are withdrawn? What limits the quantity of electricity that can be withdrawn? Give the composition of the cell when the voltage has dropped to zero, assuming that the volumes of the solutions at the two electrodes are equal.

10. In Fig. 19.6 (p. 419) why is the switch S_2 always left open, and closed only momentarily in balancing the voltages?

11. Explain the nature of the error caused in the potentiometric measurement of Fig. 19.6 if the unknown source has a resistance which is (a) very high, or (b) very low, compared to the resistance of the potentiometer.

12. How should electrochemical cells be set up to estimate the following equilibrium constants? (a) Solubility product of AgCl. (b) Equilibrium constant for the formation of $\text{Ag}(\text{NH}_3)_2^+$. (c) K_a for HAc. (d) Ionization constant of water. (e) K_b for Ac^- . (f) K_b for NH_3 . (g) K_a for NH_4^+ . (h) Equilibrium constant for the reaction between Fe^{2+} and Ag^+ . (i) Equilibrium constant for the reaction between Sn^{2+} and I_2 .

13. Devise appropriate bridges for the cells of Prob. 1, Sec. 19E (p. 434), and tell in which direction the bridge ions migrate when the cells discharge spontaneously.

14. The half-reaction $\text{AgCl} + e \rightleftharpoons \text{Ag} + \text{Cl}^-$ is the basis of a very convenient reference electrode. Design such an electrode.

15. It is desired to draw a small current from the following cell:



Describe the way in which the cell should be designed to reduce the effects of polarization. In order to answer this question, speculate upon the mechanism by which polarization occurs, and the factors upon which polarization depends.

Section 19F

1. A reducer and an oxidizer are far apart in the TSP, and the reaction tendency is high. When the two substances are mixed no appreciable reaction occurs. Discuss briefly the means which might be tried to bring about the reaction.

2. According to equilibrium considerations, how completely should hydrogen and oxygen react? Write the equation for the reaction. How may this reaction be brought about?

3. According to equilibrium considerations, how should Zn metal behave in pure water? (The rate becomes appreciable only upon boiling.)

4. According to equilibrium considerations, should 0.10 M KMnO_4 be stable in 1.0 M H_2SO_4 ? Write the equation for the decomposition.

5. According to the TSP, there are many reducers and oxidizers which should be unstable in aqueous solution. Select four known by you to be stable, and write equations for the "decomposition" reactions.

6. The following group of substances is chosen from the TSP. Discuss the reaction in acid solution of each substance with each of the others, giving attention in each case to (a) completeness of reaction, and (b) the different possibilities dependent upon which reagent of the pair is in excess. Write balanced equations only for those equilibria which lie predominantly on the side of the products. (Since more than 50 pairs are possible, the instructor should designate certain combinations.) $\text{Ti}_{(s)}, \text{Sn}^{2+}, \text{Fe}^{2+}, \text{Ce}^{3+}, \text{Mg}^{2+}, \text{H}_{2(g)}, \text{Cu}^{2+}, \text{UO}_2^{2+}, \text{NO}_3^-, \text{Cr}_2\text{O}_7^-, \text{S}_2\text{O}_8^{2-}$.

7. In working Ex. 1, page 411, the reactions of the reagents with water were completely ignored. From equilibrium considerations only, explain how important such reactions would be and write their equations. List all substances that might be present in appreciable concentrations at equilibrium.

8. In working Ex. 1, page 411, the reactions of the reagents with oxygen from the air were completely neglected. From equilibrium considerations only, explain how important such reactions would be and write their equations. List all substances that might be present in appreciable concentrations at equilibrium.

9. In the cell of Ques. 2b, Sec. 19E (p. 429), explain in detail what would happen if an iron electrode were substituted for the platinum and if the cell were then allowed to discharge to equilibrium.

10. In Ex. 1, page 421, suppose that MCl^+ is formed, at a concentration approximately equal to that of M^{2+} . Describe the error of the solubility product calculated as in Ex. 1. Describe the error if the concentration of MCl^+ is of the same order as that of KCl .

11. Explain why the answer to Prob. 5a, Sec. 19D (p. 433), has no meaning in reality.

12. Study the three half-reactions that involve copper, at 0.521, 0.337, and 0.153 v in the TSP, and then criticize or defend the statement that Cu^+ is a better oxidizer than Cu^{2+} .

13. Study the three half-reactions *a*, *c*, and *f* in Exs. 3 and 4 (p. 426), and then criticize or defend the statement that N_2O_4 is a stronger oxidizer than HNO_3 .

PROBLEMS

Section 19C

Problems in stoichiometry that involve common redox methods may be found at the end of Chapter 20.

1. For each of the following solutions, find (a) the equivalent weight, and (b) the molarity of a 0.1200 *N* solution. Cd metal (as a reducer); HNO_2 (as a reducer); Cl_2 (as an oxidizer); H_2O_2 (as a reducer); TiOSO_4 ; H_2S (oxidized to free sulfur); SO_2 (oxidized to H_2SO_4); $\text{Na}_2\text{S}_2\text{O}_8$ (reduced to SO_4^{2-}); H_3AsO_4 ; UO_2SO_4 ; $\text{K}_2\text{Cr}_2\text{O}_7$.
Ans. 23.507; 0.0600 *M* (for HNO_2).

2. For a solution of each of the substances in Prob. 1, what is the normality of a 0.0800 *M* solution? The molarity of a 0.100 *N* solution? The titer of a 0.200 *M* solution?
Ans. 0.1600 *N*; 0.0500 *M*; 9.40 mg/ml (for HNO_2).

3. How many grams of each substance in Prob. 1 are required for 300 ml of 0.150 *N* solution? For 500 ml of 0.200 *M* solution?
Ans. 1.06 g; 4.70 g (for HNO_2).

4. Give the amount of substance in column 2 that is equivalent to the sample in column 1.

Column 1	Column 2
(a) 27.23 ml 0.1025 <i>N</i> KMnO ₄	776 mg FeSO ₄ ·7H ₂ O
(b) 53.6 mg As ₂ O ₃	_____ml 0.1200 <i>N</i> KMnO ₄
(c) 0.1675 g CaC ₂ O ₄	_____ml 0.250 <i>N</i> KMnO ₄
(d) 46.50 ml 0.100 <i>M</i> H ₂ S	_____ml 0.1500 <i>M</i> KMnO ₄
(e) 165 mg KNO ₂	_____ml 0.200 <i>N</i> Ce(SO ₄) ₂
(f) 26.50 ml 0.0625 <i>M</i> Na ₃ AsO ₃	_____ml 0.1500 <i>M</i> Ce(SO ₄) ₂
(g) 14.52 ml 0.125 <i>M</i> AgNO ₃	_____mg metallic Zn
(h) 293 mg Ti ₂ SO ₄	_____ml 0.200 <i>M</i> Ce(SO ₄) ₂
(i) 342 mg FeSO ₄	_____ml 0.0500 <i>M</i> K ₂ Cr ₂ O ₇
(j) 183 mg iodine	_____mg As ₂ O ₃

5. All the metal in each of the compounds of column 1 is converted to the oxidation state shown in column 2. The metal is then determined volumetrically as outlined by the unbalanced equations in column 3. Complete the table by adding three more columns: in column 4, write the equivalents per mole of the compound; in column 5, give the equivalent weight of the compound; in column 6, give the titer of the 0.2000 *N* standard solution used in titration, in terms of the sought-for compound.

Compound	Converted to	Reactions for Determination
(a) Fe ₂ O ₃	Fe ²⁺	Fe ²⁺ + MnO ₄ ⁻ (stand.) → Fe ³⁺ + Mn ²⁺
(b) As ₂ O ₃	H ₃ AsO ₃	H ₃ AsO ₃ + I ₂ (stand.) → H ₃ AsO ₄ + I ⁻
(c) Cr ₂ O ₃	Cr ₂ O ₇ ⁼	Cr ₂ O ₇ ⁼ + Fe ²⁺ (stand.) → Cr ³⁺ + Fe ³⁺
(d) Na ₂ UO ₄	U ⁴⁺	U ⁴⁺ + MnO ₄ ⁻ (stand.) → UO ₂ ²⁺ + Mn ²⁺
(e) Ce ₂ O ₃	Ce ⁴⁺	Ce ⁴⁺ + Fe ²⁺ (stand.) → Ce ³⁺ + Fe ³⁺
(f) CaCO ₃	Ca ²⁺	Ca ²⁺ + C ₂ O ₄ ⁼ (excess) → CaC ₂ O ₄ (filter, wash)
		CaC ₂ O ₄ + H ⁺ (excess) → Ca ²⁺ + H ₂ C ₂ O ₄
		H ₂ C ₂ O ₄ + MnO ₄ ⁻ (stand.) → CO ₂ + Mn ²⁺
(g) CuO.....	Cu ²⁺	Cu ²⁺ + I ⁻ (excess) → CuI + I ₂
		I ₂ + S ₂ O ₃ ⁼ (stand.) → I ⁻ + S ₄ O ₆ ⁼
(h) Ba ₃ (PO ₄) ₂	Ba ²⁺	Ba ²⁺ + CrO ₄ ⁼ (excess) → BaCrO ₄ (filter, wash)
		BaCrO ₄ + H ⁺ (excess) → Ba ²⁺ + Cr ₂ O ₇ ⁼
		Cr ₂ O ₇ ⁼ + Fe ²⁺ (stand.) → Cr ³⁺ + Fe ³⁺
(i) Mo ₂ O ₃	Mo ³⁺	Mo ³⁺ + MnO ₄ ⁻ (stand.) → MoO ₄ ⁼ + Mn ²⁺
(j) V ₂ O ₅	VO ²⁺	VO ²⁺ + MnO ₄ ⁻ (stand.) → VO ₂ ⁺ + Mn ²⁺

Ans. (g) 1; 79.54 g; 15.908 mg CuO/ml.

6. The acid-base normality of an HNO₃ solution is 0.2000 *N*. What would be its redox normality, assuming that the product is NO? Is it accurate to make this assumption? Explain.

7. What is the ratio of the acid-base equivalent weight to the redox equivalent weight for H₂C₂O₄? For KHC₂O₄·H₂C₂O₄? Ans. 1:1; 4:3.

8. What is the composition of the resulting mixture if 0.400 mole of K₂Cr₂O₇ is added to an aqueous solution containing 2.00 moles of VSO₄ and 8.00 moles of H₂SO₄? (Hint: From the TSP, dichromate is capable of oxidizing V(II) to V(III), V(IV), or V(V). The products actually formed will depend on the original amount of dichromate compared to the original amount of V(II).)

9. Write the equations for the action of excess Sn metal on Cr₂O₇⁼, and for the action of excess Cr₂O₇⁼ on Sn metal. (a) Calculate the moles of Sn²⁺ and of Sn⁴⁺ formed when 3.00 moles of metallic Sn are mixed with 1.25 moles of Cr₂O₇⁼. (b) In what range of mole ratios may Sn metal and K₂Cr₂O₇ be mixed to give a mixture containing Sn²⁺ and Sn⁴⁺, but no metallic Sn?

Ans. (a) 2.25 moles Sn²⁺, and 0.75 mole Sn⁴⁺.

Section 19D

1. Write the expressions for the E 's of the following half-reactions, representing the standard single-electrode potential in each case by the symbol E° .

- $\text{Tl}^{3+} + 2e \rightleftharpoons \text{Tl}^+$
- $\text{Pb}^{2+} + 2e \rightleftharpoons \text{Pb}_{(s)}$
- $\text{Ag}_2\text{S}_{(s)} + 2\text{H}^+ + 2e \rightleftharpoons 2\text{Ag}_{(s)} + \text{H}_2\text{S}_{(g)}$
- $\text{H}_3\text{AsO}_4 + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_3\text{AsO}_3 + \text{H}_2\text{O}$
- $\text{Cl}_{2(g)} + 2e \rightleftharpoons 2\text{Cl}^-$
- $\text{IO}_3^- + 6\text{H}^+ + 5e \rightleftharpoons \frac{1}{2}\text{I}_{2(s)} + 3\text{H}_2\text{O}$

$$\text{Ans. (c) } E^\circ + \frac{0.0591}{2} \log \frac{[\text{H}^+]^2}{P_{\text{H}_2\text{S}}}$$

2. Calculate E for each of the following systems.

- $\text{Cd}_{(s)}; 0.010 \text{ M CdSO}_4$
- $\text{Ag}_{(s)}; 0.010 \text{ M KAg(CN)}_2, 0.010 \text{ M KCN}$
- $\text{Ag}_{(s)}; \text{AgBr}_{(s)}, 0.0010 \text{ M KBr}$
- $\text{Pt}; 0.020 \text{ M K}_4\text{Fe(CN)}_6, 0.0010 \text{ M K}_3\text{Fe(CN)}_6$
- $\text{Cu}_{(s)}; 0.010 \text{ M CuSO}_4$
- $\text{Pt}; 0.015 \text{ M UO}_2\text{SO}_4, 0.050 \text{ M U(SO}_4)_2, 0.010 \text{ M H}_2\text{SO}_4$
- $\text{Pt}; 0.010 \text{ M FeSO}_4, 0.010 \text{ M Fe}_2(\text{SO}_4)_3$
- $\text{Pt}; \text{H}_2 (0.30 \text{ atm}), 0.075 \text{ M HCl}$
- $\text{Pt}; 0.010 \text{ M TiOSO}_4, 0.010 \text{ M Ti}_2(\text{SO}_4)_3, 0.10 \text{ M H}_2\text{SO}_4$
- $\text{Hg}_{(l)}; \text{Hg}_2\text{Cl}_{2(s)}, 0.10 \text{ M KCl}$
- $\text{Pt}; \text{O}_2 (0.2 \text{ atm}), 0.10 \text{ M HCl}, 0.010 \text{ M H}_2\text{O}_2$
- $\text{Pt}; 0.010 \text{ M K}_2\text{Cr}_2\text{O}_7, 0.010 \text{ M Cr}_2(\text{SO}_4)_3, 0.020 \text{ M H}_2\text{SO}_4$

$$\text{Ans. (b) } -0.19 \text{ v; (e) } 0.278 \text{ v.}$$

3. A solution is 0.10 M each in Mn^{2+} and MnO_4^- . Calculate E in this solution when $[\text{H}^+] = 1.00 \text{ M}$. When $[\text{H}^+] = 1.0 \times 10^{-4} \text{ M}$. Ans. $1.51 \text{ v}; 1.13 \text{ v}$.

4. A solution is 0.10 M each in H^+ and Mn^{2+} . What must be $[\text{MnO}_4^-]$ in order that $E = 0 \text{ v}$?

5. The following single-electrode systems are each at an E of -0.105 v . Express the concentrations designated as x .

- $\text{Pt}; 0.030 \text{ M Fe}^{2+}, x \text{ M Fe}^{3+}$
- $\text{Pt}; \text{H}_2 (1 \text{ atm}), x \text{ M H}^+$
- $\text{Pt}; 1.0 \text{ M Ti}^{3+}, 1.0 \text{ M H}^+, x \text{ M TiO}^{2+}$
- $\text{Pt}; 0.10 \text{ M CrO}_4^{2-}, \text{Cr(OH)}_3(s), x \text{ M OH}^-$
- $\text{Ag}_{(s)}; x \text{ M Ag}^+$
- $\text{Pt}; 0.010 \text{ M UO}_2\text{SO}_4, 0.020 \text{ M U(SO}_4)_2, x \text{ M H}^+$
- $\text{Ag}_{(s)}; \text{AgI}_{(s)}, x \text{ M I}^-$
- $\text{Pt}; \text{Fe(OH)}_2(s), \text{Fe(OH)}_3(s), x \text{ M OH}^-$

$$\text{Ans. (a) } 4.4 \times 10^{-17} \text{ M.}$$

6. From the E° for the $\text{Ag}^+ - \text{Ag}_{(s)}$ half-reaction, and the solubility product of Ag_2CrO_4 , calculate E° for the half-reaction $\text{Ag}_2\text{CrO}_{4(s)} + 2e \rightleftharpoons 2\text{Ag}_{(s)} + \text{CrO}_4^{2-}$.

7. From the E° values of the half-reactions $\text{Ag}^+ + e \rightleftharpoons \text{Ag}_{(s)}$ and $\text{AgBr}_{(s)} + e \rightleftharpoons \text{Ag}_{(s)} + \text{Br}^-$, calculate the solubility product of AgBr , and compare with the value in Appendix V. Ans. 1.2×10^{-12} .

8. Calculate E° for the reaction $\text{Cd(CN)}_4^{2-} + 2e \rightleftharpoons \text{Cd}_{(s)} + 4\text{CN}^-$, and compare it with E° for the reaction $\text{Cd}^{2+} + 2e \rightleftharpoons \text{Cd}_{(s)}$.

9. The following systems are made up to contain the designated components, and reaction takes place in each case. Tell in what direction each component changes, but do not calculate the extent of the change.

- $\text{Ag}_{(s)}$, $0.1\text{ }M\text{ Fe}^{3+}$, $0.01\text{ }M\text{ Ag}^+$, $10^{-3}\text{ }M\text{ Fe}^{2+}$
- $0.1\text{ }M\text{ Fe}^{2+}$, $0.1\text{ }M\text{ Cu}^{2+}$, $0.1\text{ }M\text{ I}^-$, $0.001\text{ }M\text{ Fe}^{3+}$, $\text{CuI}_{(s)}$
- $\text{Sn}_{(s)}$, $0.05\text{ }M\text{ Pb}^{2+}$, $0.11\text{ }M\text{ Sn}^{2+}$, $\text{Pb}_{(s)}$
- $0.010\text{ }M\text{ Ti}^{3+}$, $\text{Cd}_{(s)}$, $0.12\text{ }M\text{ TiO}^{2+}$, $0.2\text{ }M\text{ Cd}^{2+}$
- $\text{Pb}_{(s)}$, $0.10\text{ }M\text{ V}^{3+}$, $10^{-3}\text{ }M\text{ Pb}^{2+}$, $10^{-2}\text{ }M\text{ V}^{2+}$
- $10^{-6}\text{ }M\text{ MnO}_4^-$, $10^{-6}\text{ }M\text{ Fe}^{2+}$, $0.2\text{ }M\text{ Mn}^{2+}$, $0.3\text{ }M\text{ Fe}^{3+}$, $pH\ 4$

Ans. (a) Fe^{3+} and $\text{Ag}_{(s)}$ decrease; Fe^{2+} and Ag^+ increase.

10. Calculate the equilibrium constants for the following unbalanced over-all reactions in acid solution.

- $\text{Fe}^{2+} + \text{Br}_{2(l)} \rightleftharpoons \text{Fe}^{3+} + \text{Br}^-$
- $\text{Cr}^{3+} + \text{Fe}_{(s)} \rightleftharpoons \text{Fe}^{2+} + \text{Cr}^{2+}$
- $\text{O}_{2(g)} + \text{H}_3\text{AsO}_3 \rightleftharpoons \text{H}_2\text{O} + \text{H}_3\text{AsO}_4$
- $\text{HNO}_2 + \text{MnO}_4^- \rightleftharpoons \text{NO}_3^- + \text{Mn}^{2+}$
- $\text{Cr}_2\text{O}_7^{2-} + \text{VO}^{2+} \rightleftharpoons \text{Cr}^{3+} + \text{VO}_2^+$
- $\text{Pb}^{2+} + \text{Cd}_{(s)} \rightleftharpoons \text{Pb}_{(s)} + \text{Cd}^{2+}$
- $\text{S}_2\text{O}_3^{2-} + \text{I}_3^- \rightleftharpoons \text{S}_4\text{O}_6^{2-} + \text{I}^-$
- $\text{Fe}(\text{CN})_6^{3-} + \text{Sn}^{2+} \rightleftharpoons \text{Fe}(\text{CN})_6^{4-} + \text{Sn}^{4+}$
- $\text{Fe}^{3+} + \text{U}^{4+} \rightleftharpoons \text{Fe}^{2+} + \text{UO}_2^{2+}$
- $\text{Cu}^+ \rightleftharpoons \text{Cu}_{(s)} + \text{Cu}^{2+}$
- $\text{Hg}_{(l)} + \text{HgCl}_2 \rightleftharpoons \text{Hg}_2\text{Cl}_{2(s)}$
- $\text{AgBr}_{(s)} + \text{H}_2\text{SO}_3 \rightleftharpoons \text{Ag}_{(s)} + \text{Br}^- + \text{SO}_4^{2-}$

Ans. (a) 9.5×10^4 (for $[\text{Fe}^{3+}][\text{Br}^-]/[\text{Fe}^{2+}]$); (l) 0.0029.

11. A system is originally $0.010\text{ }M$ in AgNO_3 and contains excess Cd metal. What are the composition and E of the solution at equilibrium?

Ans. $[\text{Ag}^+] = 3 \times 10^{-22}\text{ }M$; $[\text{Cd}^{2+}] = 0.0050\text{ }M$;
 $[\text{NO}_3^-] = 0.010\text{ }M$; -0.471 v .

12. An excess of Fe metal is placed in $0.0035\text{ }M\text{ CdSO}_4$. What is $[\text{Cd}^{2+}]$ at equilibrium?

13. A $0.10\text{ }M$ solution of ferric ion is shaken with solid Ag until equilibrium is attained. Calculate the percentage of iron that remains unreduced. *Ans.* 19%.

14. Repeat Prob. 13, if the solution also contains $1.0\text{ }M\text{ HCl}$. (Neglect complexing of Fe^{3+} by the Cl^- .)

15. There are mixed 50.0 ml each of $0.0150\text{ }M\text{ SnSO}_4$, $0.0150\text{ }M\text{ K}_2\text{Cr}_2\text{O}_7$, and $0.116\text{ }M\text{ H}_2\text{SO}_4$. Calculate the composition and E of the system at equilibrium.

Ans. $0.00333\text{ }M\text{ K}_2\text{Cr}_2\text{O}_7$; $0.00500\text{ }M\text{ Sn}(\text{SO}_4)_2$; $0.00167\text{ }M\text{ Cr}_2(\text{SO}_4)_3$;
 $0.00167\text{ }M\text{ K}_2\text{SO}_4$; $8 \times 10^{-38}\text{ }M\text{ SnSO}_4$; $0.0270\text{ }M\text{ H}_2\text{SO}_4$; 1.18 v .

16. There are mixed 50.0 ml each of $0.0250\text{ }M\text{ K}_2\text{Cr}_2\text{O}_7$, $0.0250\text{ }M\text{ CrSO}_4$, and $0.190\text{ }M\text{ H}_2\text{SO}_4$. Calculate the composition and E of the system at equilibrium.

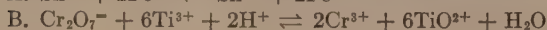
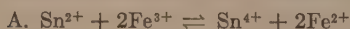
17. An acid $0.010\text{ }M$ solution of Fe^{2+} is allowed to stand in air. What percentage of the Fe^{2+} remains unoxidized, if $[\text{H}^+] = 0.10\text{ }M$, and if $P_{\text{O}_2} = 0.20\text{ atm}$ at equilibrium?

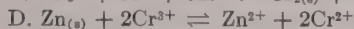
Ans. $2.6 \times 10^{-5}\%$.

18. Repeat Prob. 17, if the solution contains $0.010\text{ }M\text{ Tl}^+$ instead of Fe^{2+} .

Section 19E

1. Draw diagrams of cells in which each of the following reactions can take place spontaneously. For each cell, with all ion concentrations at $0.0020\text{ }M$, designate the following: (a) The reaction at each electrode. (b) Voltage of the cell. (c) Polarity of the electrodes. (d) The direction in which electrons flow in the external circuit.





Ans. For cell A: (a) $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$ (cathode), $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$ (anode); (b) 0.62 v; (c) cathode is positive, anode is negative; (d) from anode to cathode.

2. Combine the single-electrode systems of Prob. 2, Sec. 19D (p. 433), in pairs to form electrochemical cells. For each cell, if it is allowed to discharge spontaneously, designate the following: (a) Reaction at each electrode. (b) Anode, cathode, and polarity of each. (c) Direction of flow of electrons in the external circuit. (d) Voltage. (e) Balanced equation for the over-all reaction. (f) Coulombs that flow per mole of reducer oxidized. (g) Maximum electrical work obtainable per mole of reducer oxidized. (Since more than 50 cells are possible, the instructor should assign certain pairs.)

Ans. For electrodes *b* and *e*: (a, b) At positive Cu cathode, $\text{Cu}^{2+} + 2e \rightarrow \text{Cu}_{(s)}$; at negative Ag anode, $\text{Ag}_{(s)} + 2\text{CN}^- \rightarrow \text{Ag}(\text{CN})_2^- + e$; (c) from anode to cathode; (d) 0.47 v; (e) $\text{Cu}^{2+} + 2\text{Ag}_{(s)} + 4\text{CN}^- \rightarrow \text{Cu}_{(s)} + 2\text{Ag}(\text{CN})_2^-$; (f) 96,496; (g) 4.5×10^4 joules.

3. From the measured voltage, V , of each of the following cells, calculate the E of the left-hand, unknown single-electrode system with respect to the standard hydrogen electrode.

- Unknown single electrode || saturated calomel electrode (negative)
- Unknown single electrode || saturated calomel electrode (positive)
- Unknown single electrode || $[\text{H}^+] = 0.010 M$; H_2 (1 atm); Pt (negative)
- Unknown single electrode || $0.010 M \text{ HCl}$; H_2 (0.10 atm); Pt (negative)
- Unknown single electrode || $0.0010 M \text{ NaCl}$, $\text{AgCl}_{(s)}$; Ag (positive)

Ans. (a) $0.246 + V$ volts.

4. Calculate the voltage of the following cell: Pt; O_2 (0.20 atm), $0.010 M \text{ HClO}_4$ || $0.010 M \text{ CuSO}_4$; Cu.

(a) The cell is permitted to discharge spontaneously (i.e., Cu metal dissolves) by connecting the electrodes together directly with a conducting wire. Designate: the reaction at each electrode, the anode and cathode, and the direction in which electrons flow in the external circuit.

(b) The process in part *a* above can be made to reverse, and Cu may be made to deposit as metal, if the positive terminal of a 1.5-v battery is connected to the Pt electrode, and the negative terminal to the Cu electrode. Designate: the reaction at each electrode, the anode and cathode, and the direction in which electrons flow in the external circuit.

5. An electrochemical cell (Cd ; CdSO_4 || CuSO_4 ; Cu) operates for a length of time such that 0.765 g of Cu is deposited. How much Cd is put into solution during this time?

Ans. 1.354 g.

6. What weights of the following metals would be deposited by 2.16 ma flowing for 2600 seconds? (a) Ag; (b) Hg (from Hg^{2+}); (c) Bi (from BiO^+).

Ans. (a) 6.28 mg.

7. How long would a constant current of 1.00 ma have to flow to deposit 1.00 mg of each of the following metals? (a) Au (from Au^{3+}); (b) Cd; (c) Zn; (d) Pb (from Pb^{2+}).

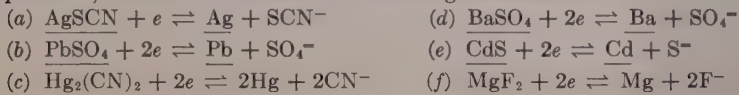
Ans. (a) 24.5 minutes.

8. What is the average cell voltage if 2500 joules are supplied by the decomposition of 0.2387 equivalents of the oxidized (or reduced) substance?

9. (a) What is the equilibrium composition of the cell of Ex. 3, page 421? (b) What is the equilibrium voltage? (c) What is the equilibrium E of each electrode?

Ans. (a) Zn compartment builds to $0.084\text{ }M\text{ }Zn^{2+}$, and Ag compartment drops to $1.1 \times 10^{-27}\text{ }M\text{ }Ag^+$.

10. With E° values for the simple metal-metal ion half-reactions (i.e., $M^{n+} + ne \rightleftharpoons M_{(s)}$) from Appendix IX, and appropriate solubility-product values from Appendix V, calculate E° values for the following half-reactions.



Ans. (c) -0.37 v.

11. From E° values in Appendix IX, calculate the solubility products or dissociation constants for the following substances: (a) $AgCl$, (b) CuI , (c) $Mg(OH)_2$, (d) $Ag(CN)_2^-$.

Ans. (c) 1.5×10^{-11} .

12. From the value of E° for the standard hydrogen electrode, and the value for the ion product of water, calculate E° for the half-reaction $2H_2O + 2e \rightleftharpoons H_{2(g)} + 2OH^-$, and check with Appendix IX.

13. What are the voltages of the following cells, if $K_a = 2.5 \times 10^{-5}$? Clearly state all necessary assumptions.

- (a) $Pt, H_2 (1\text{ atm}); 0.080\text{ }M\text{ }HA \parallel \text{standard hydrogen electrode}$
- (b) $Pt, H_2 (1\text{ atm}); 0.040\text{ }M\text{ }HA, 0.030\text{ }M\text{ }NaA \parallel \text{normal calomel electrode}$
- (c) $Pt, H_2 (1\text{ atm}); 0.080\text{ }M\text{ }NaA \parallel \text{saturated calomel electrode}$

Ans. (a) 0.1685 v.

14. What are the voltages of the following cells, if $K_b = 2.0 \times 10^{-5}$ for the weak monoequivalent base, B? Clearly state all necessary assumptions.

- (a) $Pt, H_2 (1\text{ atm}); 0.050\text{ }M\text{ }B \parallel \text{saturated calomel electrode}$
- (b) $Pt, H_2 (1\text{ atm}); 0.050\text{ }M\text{ }B, 0.030\text{ }M\text{ }BHCl \parallel \text{standard hydrogen electrode}$
- (c) $Pt, H_2 (1\text{ atm}); 0.025\text{ }M\text{ }BHCl \parallel \text{saturated calomel electrode}$

Ans. (a) 0.896 v.

15. Calculate the acid ionization constants for the weak monoprotic acids from the given voltages (V) of the following electrochemical cells.

(a) $Pt, H_2 (1\text{ atm}); 0.0100\text{ }M\text{ }HA \parallel \text{standard hydrogen electrode (positive); } V = 0.212\text{ v}$

(b) $Pt, H_2 (1\text{ atm}); 0.020\text{ }M\text{ }NaA \parallel \text{normal calomel electrode (positive); } V = 0.822\text{ v}$

(c) $Pt, H_2 (1\text{ atm}); 0.030\text{ }M\text{ }HA, 0.100\text{ }M\text{ }NaA \parallel \text{saturated calomel electrode (positive); } V = 0.550\text{ v}$

Ans. (a) 6.8×10^{-6} .

16. Calculate the basic ionization constants for the weak monoequivalent bases from the given voltages of the following electrochemical cells.

(a) $Pt, H_2 (1\text{ atm}); 0.020\text{ }M\text{ }B \parallel \text{normal calomel electrode (positive); } V = 0.795\text{ v}$

(b) $Pt, H_2 (1\text{ atm}); 0.040\text{ }M\text{ }BHCl \parallel \text{standard hydrogen electrode (positive); } V = 0.305\text{ v}$

(c) $Pt, H_2 (1\text{ atm}); 0.030\text{ }M\text{ }B, 0.020\text{ }M\text{ }BHCl \parallel \text{saturated calomel electrode (positive); } V = 0.721\text{ v}$

Ans. (a) 1.14×10^{-9} .

17. E° for the $M^{3+}-M_{(s)}$ half-reaction is -0.093 v. Calculate the solubility product for MCl_3 if the voltage of the following cell is 0.240 v. the standard electrode being positive.

$M; MCl_{3(s)}, 0.030\text{ }M\text{ }CaCl_2 \parallel \text{standard hydrogen electrode}$

Ans. 7.4×10^{-12} .

18. E° for the $M^+-M_{(s)}$ half-reaction is 0.387 v. Calculate the dissociation constant of the soluble complex MCl , if the voltage of the following cell is 0.163 v, and the M electrode is positive.

Standard hydrogen electrode \parallel 0.0100 M MNO_3 , 0.0300 M KCl ; M

Section 19F

1. In working Ex. 1, page 411, the formation of Tl^{3+} was neglected. Justify this assumption by calculating the $[Tl^{3+}]$ which must exist at the equilibrium E .

Ans. $10^{-60} M$.

2. For Ex. 1, page 425, calculate the equilibrium constant of the reaction. Predict what would be the ratio of $[Ce^{3+}]/[Ce^{4+}]$ in a solution containing 1.0 M HNO_3 and saturated with air, if $P_{O_2} = 0.20$ atm.

3. From the E calculated in Prob. 2e (p. 433), calculate the $[Cu^+]$ that must be formed according to the reaction $Cu^{2+} + Cu_{(s)} \rightleftharpoons 2Cu^+$. If $[Cu^+]$ were appreciable compared to $[Cu^{2+}]$, how would the answer given for Prob. 2e be in error?

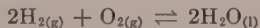
Ans. $7.7 \times 10^{-5} M$; answer of 0.278 v would be too high.

4. Calculate E for the system of Prob. 2k (p. 433). Also calculate E for the O_2 - H_2O half-reaction ($E^\circ = 1.229$ v), and compare with the answer of Prob. 2k. If the system were allowed to reach equilibrium, what would be the H_2O_2 concentration, if the oxygen and HCl concentrations remained unchanged? In the light of the answer, how stable is H_2O_2 ?

5. If a 0.010 M solution of $FeSO_4$ at pH 7 is treated with pure iron, should any hydrogen be evolved? Below what pH should hydrogen gas be liberated at a pressure of 1 atm or more?

Ans. Yes; 8.44.

6. Calculate the equilibrium constant for the reaction



Explain why a mixture of hydrogen and oxygen is "stable" at room temperature, and describe the ways in which such a mixture may be brought to equilibrium.

20 REDOX TITRATIONS

20A. INTRODUCTION

Because so many elements may be easily oxidized or reduced, more titration methods are based on redox reactions than on any other type of reaction. Only a few standard solutions are used, but a great variety of substances may be determined with each; for example, the substances directly or indirectly titratable with standard KMnO_4 are listed in Table 20.3 (p. 456).

This chapter describes the general theory and performance of redox titrations. Some common methods are outlined and a few experiments are given. An understanding of Chapter 19 is prerequisite.

20A.1. Requirements of a Volumetric Redox Reaction

A good redox reaction must generally satisfy the requirements listed on page 229. The requirement of a single, stoichiometric reaction is somewhat difficult to meet in redox titrations, because the substances involved may go to more than one other oxidation state, or because of side or induced reactions.

If a particular oxidizer may go to more than one reduced state, it will be useless as a standard oxidizing agent unless conditions are selected to make it go exclusively to only one lower oxidation state. Thus KMnO_4 is not a good standard oxidizing agent at intermediate acidity, since it goes partially to Mn(II) and partially to MnO_2 . However, KMnO_4 is suitable under restricted conditions, for it may be made to go exclusively to Mn(II) in fairly acid solution, or exclusively to MnO_2 in nearly neutral solutions.

Error will also arise if the oxidizing or reducing agent undergoes side reactions. A standard oxidizer or reducer may react not only with the sought-for substance, but also with other oxidizable or reducible substances that may be present in the system. Some strong oxidizers or reducers react with water itself. Some reducers may react with air. As an example, it is often desired to determine Fe(II) in solutions containing chloride by titration with a standard oxidizing agent. If the oxidizer is too strong, not only is the sought-for Fe(II) oxidized, but so is chloride.



By a proper choice of standard oxidizing agent, however, it is possible to determine Fe(II) without side-oxidation of chloride.

Induced reactions as a source of error are discussed in the Supplement (p. 812).

20A.2. Standard Solutions. Primary Standards

The oxidizing agents most commonly used in standard titrating solutions are KMnO_4 , cerate, iodine, and $\text{K}_2\text{Cr}_2\text{O}_7$. These and others are discussed in greater detail later in this chapter. Most standard reducing solutions are less stable and less convenient to use than standard oxidizing solutions, and, with the exception of $\text{Na}_2\text{S}_2\text{O}_3$ and FeSO_4 , relatively few determinations are based on titration with standard reducing solutions.

A wide variety of substances is used as primary standards. Following are a few substances whose reagent grades may be used as primary standards with little preparation other than drying. Greater detail on the preparation and use of these substances and others may be found in the literature (K19, U4).

20A.2a. Primary standard reducing agents. Arsenious oxide (As_2O_3 , eq. wt. 49.46) is used to standardize iodine, KMnO_4 , and cerate solutions. The reagent-grade chemical is very pure, since it is sublimed in manufacture. Primary standard As_2O_3 that has been prepared and analyzed carefully is available from the National Bureau of Standards. As_2O_3 is not rapidly soluble except in basic (NaOH or Na_2CO_3) solutions. The acidified solution is fairly stable in air, and may be used as a standard titrant.

Sodium oxalate ($\text{Na}_2\text{C}_2\text{O}_4$, eq. wt. 67.00) is used to standardize KMnO_4 and cerate solutions. It is very stable and easy to prepare. It is also available from the NBS. $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ is also a primary standard, but is somewhat less reliable than $\text{Na}_2\text{C}_2\text{O}_4$ because of its

water of crystallization. Oxalate solutions are not very stable on storage, $\text{Na}_2\text{C}_2\text{O}_4$ being less stable than $\text{H}_2\text{C}_2\text{O}_4$.

Iron wire (Fe metal, eq. wt. 55.85) may be used to standardize many oxidizing solutions. The purest iron available is prepared electrolytically and ignited in a stream of hydrogen, which removes oxides and decreases C and P impurities. Reagent-grade Fe wire with an assay value is adequate for ordinary quantitative analysis. The iron is dissolved in acid, reduced to Fe(II), and then titrated with the oxidizing solution to be standardized.

Many other reagent-grade chemicals may be used as "primary standard" reducing agents, if errors of a few tenths of a per cent are tolerable. Among such reagents are $\text{Na}_2\text{S}_2\text{O}_3$, $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (Mohr's salt), and KI.

20A.2b. Primary standard oxidizing agents. Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$, eq. wt. 49.03) is excellent for standardizing many kinds of reducing solutions by direct titration, and also for standardizing oxidizing solutions by indirect titration. It is stable enough to be dried at 150°C , and may be used to prepare stable standard solutions. Although assayed reagent-grade material is adequate for ordinary quantitative analytical purposes, even more reliable material may be purchased from the NBS.

Iodine (eq. wt. 126.90) is prepared by sublimation during manufacture, and the reagent-grade material is a good primary standard. It must be weighed in a closed container because of its volatility and corrosiveness. It is used principally to prepare standard iodine solutions, and to standardize $\text{Na}_2\text{S}_2\text{O}_3$ solutions. Iodine is not very soluble in water, but dissolves readily in KI solutions.

Potassium iodate (KIO_3 , eq. wt. 35.67) in reagent-grade form is a suitable primary standard for ordinary analytical purposes. It may also be used as an acidimetric primary standard. The low equivalent weight is a slight disadvantage.

Other primary standard oxidizing agents are KBrO_3 , electrolytic Cu, and $\text{K}_3\text{Fe}(\text{CN})_6$.

20A.3. Preoxidation or Prereduction

After a sought-for substance has been put into solution and interferences have been removed, it will not usually be in the oxidation state required for titration, and may in fact exist in several oxidation states. It is, therefore, almost always necessary to convert the sought-for substance quantitatively into a particular oxidation state prior to titration. This process is called *preoxidation* or *prereduction*, and is usually carried out with an excess of the preoxidant or prereductant. Before titration

it is essential to remove or inactivate all excess preoxidant or prereductant; if this is not done, the excess may react with the standard titrating solution and be mistaken for the sought-for substance. A few of the ways in which the excess of preoxidant or prereductant may be removed before titration are described in the following two paragraphs.

Consider, as an example, the determination of Mn in an ore. When the sample is dissolved, most of the Mn goes into solution as Mn(II). The Mn(II) may be quantitatively preoxidized to Mn(VII) with excess sodium bismuthate (NaBiO_3) as a preoxidant. The Mn(VII) may then be determined by titration with standard FeSO_4 . Before titration, however, the excess NaBiO_3 must be removed, or it will cause error by oxidizing the standard FeSO_4 . The NaBiO_3 may be easily removed by filtration, since it is insoluble.

In a few special cases, the excess preoxidant or prereductant does not react at an appreciable rate with the standard titrant, and the excess need not be removed before titration. HClO_4 is such an oxidant; in hot concentrated solution it is a powerful oxidant, but at room temperature in dilute solution, it has no oxidizing power at all. In other cases, where the preoxidant or prereductant is of considerably different strength than the sought-for substance, it may be possible to titrate the excess selectively in the presence of the sought-for substance to a first potentiometric end point, and then to continue the titration to a second end point corresponding to the sought-for substance. Sn(II) may be used in this way as a prereductant for Fe (p. 473).

Preoxidants or prereductants are usually strong ones, selected primarily for the ease with which the excess may be removed or inactivated before titration. Some common preoxidants are Na_2O_2 , H_2O_2 , $\text{K}_2\text{S}_2\text{O}_8$, NaBiO_3 , O_3 , and HClO_4 . These are described briefly in the Supplement (p. 818). Some common prereductants are metals and amalgams, SO_2 , and SnCl_2 (p. 820). Proper choice of the prereductant sometimes permits selective reduction of the sought-for substance alone in the presence of other reducible substances, thereby avoiding troublesome separations (p. 823). The importance of reaction rate in preoxidation is discussed on page 823.

20B. REDOX TITRATIONS

20B.1. The Course of a Redox Titration

It seems best to describe the course of a redox titration with reference to a specific example, such as the titration of FeSO_4 with $\text{Ce}(\text{SO}_4)_2$. Here the reaction is very complete, because $\text{Ce}(\text{SO}_4)_2$ is a strong oxidizer that lies well above FeSO_4 in the TSP.

Consider what happens as the standard $\text{Ce}(\text{SO}_4)_2$ is added to the FeSO_4 in the titration. At the beginning of the titration the reducing strength of the FeSO_4 solution is high, since all Fe exists as $\text{Fe}(\text{II})$. The E of the titrated solution is

$$E = E_{\text{Fe}}^\circ + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

At the beginning of the titration $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ is very small, and E is very low.* As standard $\text{Ce}(\text{SO}_4)_2$ is added, $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ becomes larger and E increases. Figure 20.1 is a titration curve showing how the E of the titrated solution depends on the volume of standard

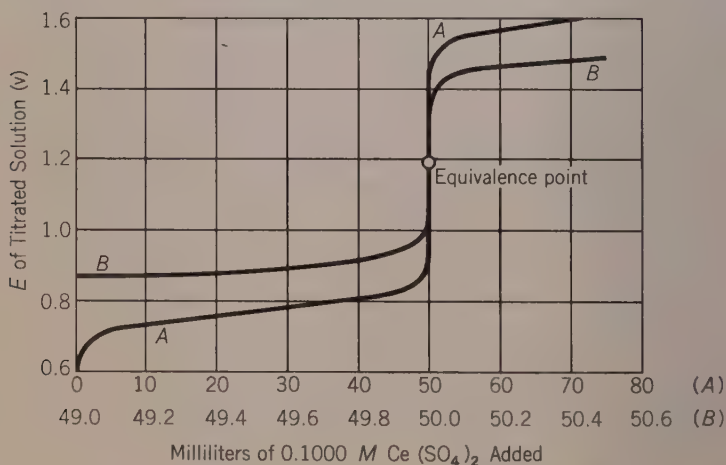


FIG. 20.1. Titration of $\text{Fe}(\text{II})$ with $\text{Ce}(\text{IV})$ —Conditions: 50.00 ml of 0.1000 M FeSO_4 titrated with 0.1000 M $\text{Ce}(\text{SO}_4)_2$. Activity and complexing effects disregarded. Volumes assumed additive. $E_{\text{Fe}}^\circ = 0.771$ v. $E_{\text{Ce}}^\circ = 1.61$ v.

$\text{Ce}(\text{SO}_4)_2$ added. (While it might be clearer to plot $p\text{Fe}^{2+}$ or $p\text{Fe}^{3+}$, E is plotted because it is the change in this quantity which is experimentally measured in a potentiometric titration.) The calculation of points on this curve is shown in the illustrative examples below.

*It might be reasoned that at the beginning of the titration, $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ is zero, and that E is infinitely low. Such low potentials are never encountered in practice. Even if there are no traces of oxidizing impurities, H^+ from water would produce a trace of $\text{Fe}(\text{III})$, giving a finite E ,



Similarly, no aqueous solution of an oxidant could have an infinitely high E ; oxidation of water would produce a trace of the reduced form, and would give a finite E .

Figure 20.1 shows that $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ and E change abruptly in the region of the equivalence point. After the equivalence point, the solution contains excess Ce(IV) , and the oxidizing power and E are high.

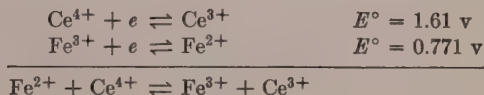
At any point in the titration the added Ce(IV) reacts with Fe(II) , producing Fe(III) and Ce(III) . At equilibrium, E may be calculated from the Nernst equation, using either the $\text{Fe}^{3+}\text{-Fe}^{2+}$ ratio (see above) or the $\text{Ce}^{4+}\text{-Ce}^{3+}$ ratio:

$$E = E_{\text{Ce}}^{\circ} + 0.0591 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]}$$

Either ratio may be used to calculate E after the addition of any volume of standard $\text{Ce(SO}_4)_2$. However, it is simpler to use the $\text{Fe}^{3+}\text{-Fe}^{2+}$ ratio before the equivalence point, and to use the $\text{Ce}^{4+}\text{-Ce}^{3+}$ ratio after, as explained in Ex. 2, below.

Example 1. Calculate the composition and E at the equivalence point in the titration of Fig. 20.1.

Since the half-reactions are so far apart in the TSP, reaction between Fe(II) and Ce(IV) is very complete. The equilibrium constant may be calculated.



At equilibrium, $E_{\text{Fe}} = E_{\text{Ce}}$, or

$$\begin{aligned} 0.771 + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} &= 1.61 + 0.0591 \log \frac{[\text{Ce}^{4+}]}{[\text{Ce}^{3+}]} \\ \frac{[\text{Fe}^{3+}][\text{Ce}^{3+}]}{[\text{Fe}^{2+}][\text{Ce}^{4+}]} &= \text{antilog} \frac{1.61 - 0.771}{0.0591} = 1.6 \times 10^{14} \end{aligned}$$

The composition at the equivalence point may be calculated. The total Fe concentration (i.e., $[\text{Fe}^{3+}] + [\text{Fe}^{2+}]$) is $0.1000 \times 50.00/100.00$, or 0.0500 M . Similarly, the total Ce concentration at the equivalence point is 0.0500 M .

At the equivalence point, let $[\text{Fe}^{2+}] = x \text{ M}$; then $[\text{Fe}^{3+}] = 0.0500 - x \text{ M}$. Since Fe^{2+} and Ce^{4+} react mole for mole, $[\text{Ce}^{3+}] = 0.0500 - x \text{ M}$ and $[\text{Ce}^{4+}] = x \text{ M}$.

Substituting these concentrations into the equilibrium expression gives

$$\frac{(0.0500 - x)(0.0500 - x)}{(x)(x)} = 1.6 \times 10^{14}$$

Solving this equation for x , assuming that $x \ll 0.0500 \text{ M}$, gives

$$x, \text{ or } [\text{Fe}^{2+}], \text{ or } [\text{Ce}^{4+}] = 4.0 \times 10^{-9} \text{ M}$$

The E at the equivalence point is

$$E = E_{\text{Fe}^\circ} + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$E = 0.771 + 0.0591 \log \frac{0.0500}{4.0 \times 10^{-9}} = 1.19 \text{ v}$$

The E calculated from the Ce concentrations is, of course, also 1.19 v.

It may be noted that the equivalence-point E is midway between the two E° values. This is generally true only when the oxidant and reductant react in equimolar ratio, and when the original solution contains no Fe^{3+} or Ce^{3+} . When these conditions are not satisfied, the equivalence-point E is not the average of the E° values. Equivalence-point E 's are calculated for other cases in the Supplement (p. 824).

Example 2. Calculate the composition and E of the solution after 40.00 ml of standard $\text{Ce}(\text{SO}_4)_2$ are added in the titration represented by Fig. 20.1.

As a first approximation, assume that the reaction between $\text{Fe}(\text{II})$ and $\text{Ce}(\text{IV})$ is practically complete, since the half-reactions are far apart in the TSP. Then, the 40.00×0.1000 , or 4.000 meq of $\text{Ce}(\text{IV})$ react to give the same number of milliequivalents of $\text{Ce}(\text{III})$, and also of $\text{Fe}(\text{III})$. Since the total milliequivalents of Fe is 5.000, the number of milliequivalents of $\text{Fe}(\text{II})$ left at equilibrium is 1.000. These amounts are in a volume of $50.00 + 40.00$, or 90.00 ml, which permits calculation of the concentrations:

$$[\text{Fe}^{3+}] = [\text{Ce}^{3+}] = \frac{4.000}{90.00} = 0.04444 \text{ M}$$

Also,

$$[\text{Fe}^{2+}] = \frac{1.000}{90.00} = 0.01111 \text{ M}$$

To calculate E ,

$$E = E_{\text{Fe}^\circ} + 0.0591 \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]}$$

$$E = 0.771 + 0.0591 \log \frac{0.04444}{0.01111} = 0.807 \text{ v}$$

$[\text{Ce}^{4+}]$ is very small, but may be calculated from the equilibrium constant of Ex. 1.

$$\frac{[\text{Fe}^{3+}][\text{Ce}^{3+}]}{[\text{Fe}^{2+}][\text{Ce}^{4+}]} = 1.6 \times 10^{14}$$

$$\frac{(0.04444)^2}{(0.01111)[\text{Ce}^{4+}]} = 1.6 \times 10^{14}$$

$$[\text{Ce}^{4+}] = 1.1 \times 10^{-15} \text{ M}$$

Note that the low concentration of $\text{Ce}(\text{IV})$ justifies the assumption of complete reaction which was made in order to estimate the concentrations of $\text{Fe}(\text{II})$, $\text{Fe}(\text{III})$, and $\text{Ce}(\text{III})$.

It may be shown that the E calculated from the concentrations of $\text{Ce}(\text{III})$ and

Ce(IV) is also 0.807 v. This method of calculating E involves more work than that given above, since $[\text{Ce}^{4+}]$ must first be calculated from the equilibrium constant. For a similar reason, it is easier to calculate E after the equivalence point from the Ce(III) and Ce(IV) concentrations, rather than from the Fe(II) and Fe(III) concentrations.

20B.2. Establishing the Equivalence Point

Inspection of Fig. 20.1 (p. 442) shows that E changes abruptly in the region of the equivalence point. It is this sharp change that permits the experimental location of the equivalence point in a titration. In general, the steeper the curve in the region of the equivalence point, the more precisely it may be located. From the way in which points on the titration curve are calculated, it should be clear that the slope of the curve in the region of the equivalence point increases as the difference increases between the E° values of the two half-reactions involved, and as the concentrations of the solutions increase.

Equivalence points are established in redox titrations by methods which may be classified conveniently into three groups: (1) potentiometric methods, (2) internal redox indicators, and (3) miscellaneous methods.

20B.2a. Potentiometric titrations. It is not possible to measure E directly in the titrated system. Experimentally, the voltage of a cell composed of two electrodes has to be measured; this voltage is a difference of two E 's. One electrode, called the *indicator electrode*, dips into the titrated solution, and forms a half-cell whose single-electrode potential (E_i) is dependent upon the concentration of the sought-for or standard substance involved in the titration. E_i changes greatly during the titration, as shown in Fig. 20.1. The other electrode, called the *reference electrode*, may either dip directly into the titrated solution or be bridged to it. The E of the reference electrode (E_r) is independent of the concentration of sought-for or standard substance, and remains constant throughout the titration. (Indicator and reference electrodes are described more fully in the Supplement, p. 827.) The experimentally measured cell voltage (V) is therefore a difference of two E 's:*

$$V = |E_i - E_r| \quad (20.1)$$

Since E_r is constant, a plot of V against volume of titrant has the same shape as a plot of E_i (Fig. 20.1), and may be used as a titration curve. The end point may be selected as the volume of titrant either at the inflection point or at a certain value of V .

*Only the absolute value of V is given. To specify the cell completely, the polarity should also be given.

Titration to the inflection point is slower than titration to a certain potential, because of the plotting required, but is usually more accurate when the titration curve is not steep. The error of titration to the inflection point is random for curves which are symmetrical about the end point. For unsymmetrical curves, there may be a determinate difference between the equivalence point and the inflection point, but this difference is only a small portion of the volume interval spanned by the steepest straight-line portion of the titration curve, and is negligible if the curve is steep.

Titration to a fixed V is faster than titration to the inflection point, and may be just as accurate for steep titration curves. The equivalence-point voltage may be calculated from Eq. 20.1. (E_i for the indicator electrode is calculable as in Ex. 1, page 443, and E_r is known.) However, such calculations should be regarded as approximations only. The calculated V generally differs from the experimental one because of (1) activity and complexing effects, and (2) junction potentials.* In practice, therefore, V for the equivalence point is always determined experimentally on a known solution of composition approximating that at the equivalence point.

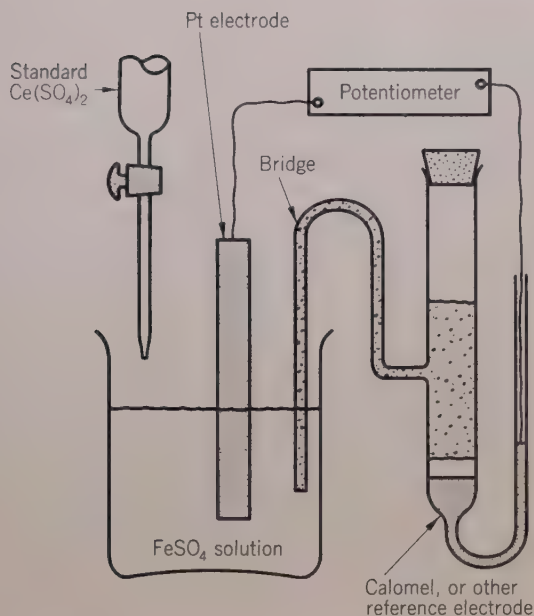
As an example, the previously mentioned titration of FeSO_4 with standard $\text{Ce}(\text{SO}_4)_2$ may be followed potentiometrically with the equipment shown in Fig. 20.2. The titration curve is obtained by plotting V (the voltage read on the potentiometer) against volume of titrant. More detail on the performance of potentiometric titrations is given in the Supplement (p. 832).

In general, when titrations are performed potentiometrically, the errors and limitations associated with chemical indicators are eliminated. Interferences are fewer, and the titrations may be performed over wider ranges of pH and ionic strength.

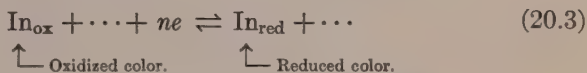
**Junction potentials* exist at the boundaries between media of dissimilar composition, and cannot in general be accurately calculated. Such potentials may occur at the boundaries between the solutions in the bridge and electrode compartments, and also between different conductor metals in the external circuit. The effect of these junction potentials is to introduce another term, E_j , into the right side of Eq. 20.1:

$$V = E_i - E_r + E_j \quad (20.2)$$

In a properly performed titration, E_j remains quite constant and does not appreciably affect the shape of the titration curve, even though it does affect the magnitude of V . Description of the magnitude and mechanism of junction potentials is beyond the scope of this text. Bates (B6) and Duke (D10) give the effects of liquid junction potentials on potentiometric methods of analysis, and describe simple methods of minimizing the effects.

FIG. 20.2. The Potentiometric Titration of FeSO_4 with $\text{Ce}(\text{SO}_4)_2$

20B.2b. Internal redox indicators. An internal redox indicator may be used in the solution being titrated. It is an organic substance which may exist in a reduced and an oxidized form, these forms having different colors.



Mechanism of the color change. As with acid-base indicators, the color of a redox indicator is due to a large number of conjugated double bonds. When such a molecule is mildly oxidized or reduced, so that it is not irreversibly split into fragments, there is sometimes a rearrangement in electronic bonding and a consequent change in color. The properties and structures of two common indicators, diphenylamine sulfonic acid and ferroin, are given in the Supplement (p. 835).

Since an internal redox indicator may be reversibly oxidized and reduced, it may be characterized by a standard potential, E° , just as any inorganic substance, and may be assigned a place in the TSP. However, the redox mechanism is complicated and may involve several steps, including proton transfers and rearrangements in bonding. Also, some redox indicators may be weak acids or bases, and the degree of ionization may depend upon pH . For these reasons, the expression of E as a function of composition is usually complicated; indicator behavior is

not fully describable by a single, simple half-reaction, and E does not follow the simple Nernst equation.

However, for a fixed set of conditions, the E of a solution containing the oxidized and reduced form of an indicator is definite and measurable. Conversely, if a trace of a particular indicator is placed in a solution whose E is determined and controlled by macroconcentrations of other oxidizing and reducing agents, the ratio of reduced to oxidized colors is fixed and definite and the proportion of oxidized color increases as the E of the solution is increased. It is therefore possible to describe the behavior of the indicator by employing the *transition potential*, which represents the E of a solution in which 50% of the indicator is in the oxidized form and 50% in the reduced form. Since this potential may depend upon acidity, ionic strength, and indicator concentration, the composition of the solution must always be given with the value of the transition potential. Table 20.1 lists several typical redox indicators and their transition potentials. Many more are described in the original references (K19). Most redox indicators transit from the reduced to the oxidized color within a range of ± 0.05 v about the transition potential (see Supplement, p. 833).

TABLE 20.1
TRANSITION POTENTIALS OF SOME INTERNAL REDOX INDICATORS*

COMMON NAME OF INDICATOR	COLOR		TRANSITION POTENTIAL (v)	CONDITIONS
	Oxidized	Reduced		
Indigo tetrasulfonate.....	blue	colorless	-0.05 0.36	pH 7 pH 0
Methylene blue.....	blue	colorless	0.01 0.53	pH 7 pH 0
Phenosafranine.....	red	colorless	-0.25 0.28	pH 7 pH 0
Phenol indophenol.....	red	colorless	0.23 0.35	pH 7 pH 5
Diphenylamine sulfonic acid..	violet	colorless	0.85	pH 0
Ferroin.....	pale blue	red	0.76 1.06	8 M H ₂ SO ₄ 0.5 M H ₂ SO ₄
Nitroferroin.....	green-blue	red	1.01 1.26	8 M H ₂ SO ₄ 0.5 M H ₂ SO ₄
Other ferroin derivatives.....	pale blue to yellow-green	red	0.70 to 1.23	0.5-8 M H ₂ SO ₄

*Data taken in part from I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, 2d ed. (New York: Wiley, 1942-57), with permission of the publisher.

Desirable properties

1. At least one of the colors should be very intense, so that only a trace of indicator is needed to give the end-point change. Otherwise the indicator blank is appreciable. Indicator solutions are rather dilute—about 0.1% in most cases—and only a few drops are generally used in a titration.

2. The color change should be sharp. The indicator must have several characteristics in order to satisfy this requirement. First, the indicator reaction 20.3 should be reversible. When this is not the case, that portion of the indicator which is changed by locally high concentrations of titrant before the equivalence point will give a premature and diffuse end point.* An advantage of a reversible change is that if the end point is overrun, the solution may be back-titrated. A second requirement for a sharp color change is that the indicator be stable in the titrated system, and not undergo side reactions. For instance, the indicator should be resistant to oxidation by air. Also, the oxidized and reduced colors should be stable in the presence of excess oxidant and reductant, and should not undergo further reactions with these reagents that might alter or bleach the color to cause fading end points.

3. The transition potential of the indicator should be insensitive to changes in pH . If the transition potential depends critically upon pH , then the pH must be rigidly controlled in order to keep the indicator blank reproducible. Precise control of pH in redox titrations is not always easy; not only do volume and ionic strength change during titration, but acid may actually be consumed or produced.

4. The indicator should be soluble in water or dilute acid solutions, and such solutions should be stable during storage. Some indicators are not very soluble in water, but may be dissolved in acid. It is not generally permissible to dissolve redox indicators in organic liquids, because these solvents or their impurities may react with the oxidizing agent used in the titration. Preparation of many indicator solutions is described in the treatise by Kolthoff and Stenger (K19).

Selection of a redox indicator. To be suitable for a particular titration an indicator must satisfy two requirements. (1) It must not react with the titrant until the sought-for substance is virtually gone. That

*Because of the requirement of reversibility, the number of useful redox indicators is not nearly so great as the number of acid-base indicators. Most organic molecules are not oxidized reversibly by oxidizing agents, but are split into fragments which cannot recombine with each other. It is only within the last two decades that most internal redox indicators have become available. Earlier there was little incentive to search for and develop them because of the large number of substances that could be determined with standard $KMnO_4$ (the color of which is its own indicator) or iodimetrically (starch being an excellent indicator).

is, the reaction tendency between titrant and sought-for substance must be much higher than the reaction tendency between titrant and indicator. If this is not the case, the end point may be premature and diffuse. (2) There must still be a high reaction tendency between the indicator and titrant, so that a very small excess of titrant past the equivalence point is sufficient to bring about the color change.

Quantitatively, the major part of the indicator transition range should be within the region of the titration curve from 0.1% before to 0.1% after the equivalence point, if a relative standard deviation of 0.1% is tolerable. In such a case, transition of the indicator is complete within the desired interval, and the titration need only be carried uncritically to a color change of the indicator. The transition potential should correspond as closely as possible to the equivalence-point potential, so that the end-point change may be sharp and accurate. Thus for the titration curve of Fig. 20.1, an indicator having a transition range within the interval 0.95–1.43 v may be used. Either ferroin (in 0.5 M H_2SO_4 , but not in 8 M H_2SO_4) or nitroferroin may be used for this titration at the 0.1% error level.

It is conceivable that an indicator might be chosen which has some of its transition range outside the region from 0.1% before to 0.1% after the equivalence point, and that the titration might then be carried to a certain color tint of the indicator. However, this technique need hardly ever be used. If the titration curve is steep enough at the equivalence point, the number of available indicators is sufficiently great to allow a choice which fulfills the requirements of the preceding paragraph. If these requirements cannot be satisfied because the titration curve is not steep enough at the equivalence point, then it is better to perform the titration potentiometrically.

20B.2c. Miscellaneous methods of establishing the equivalence point

Specific indicators. Indicator substances which react specifically with the titrant or sought-for substances are distinctly different from internal redox indicators, whose color change depends only upon the E of the solution being titrated. The best example of a specific indicator is starch, which forms an intense blue complex with iodine. Reducing agents may be titrated with standard iodine, starch being used as an indicator. Before the equivalence point the solution is colorless, since the iodine is reduced to iodide. After the equivalence point the first slight excess of iodine forms the blue starch-iodine complex. The indicator change is reversible; iodine solutions may be titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$ to the disappearance of the blue color.

Thiocyanate may be used as an indicator in the titration of Fe(III) with a strong reducer, such as TiCl_3 or CrCl_2 . The end point is indi-

cated by the disappearance of the reddish color of the ferric thiocyanate complex. (Fe(II) does not form a colored complex with thiocyanate.)

$K_3Fe(CN)_6$ may be used as a specific external indicator in the titration of Fe(II) with $K_2Cr_2O_7$. As long as the titrated solution contains Fe(II), Turnbull's blue— $Fe_3[Fe(CN)_6]_2$ —is formed with the indicator. As soon as the equivalence point is passed, the Fe(II) concentration is so low that the blue compound is not formed. Fe(III) gives no coloration with ferrieyanide.

Colored reagents that act as indicators. If the standard reagent is highly colored, and if it is decolorized by the substance being titrated, the reagent color is established as soon as a slight excess is added past the equivalence point. The only common reagent used in this way is $KMnO_4$. The excess required (i.e., indicator blank) is only a few hundredths of a milliliter of 0.1 N $KMnO_4$ in end-point volumes of 100–200 ml, but the blank becomes quite large when 0.01 N $KMnO_4$ is used.

Some common reagents are not colored intensely enough to serve precisely as indicators, but they are colored sufficiently to allow an estimation of the end point. This property is often useful in titrations. For example, in the prereduction of $FeCl_3$ to $FeCl_2$ with $SnCl_2$ prior to titration with $KMnO_4$, a large excess of $SnCl_2$ must be avoided. $FeCl_3$ has an intense yellow color in conc. HCl, and the disappearance of this color indicates that the proper amount of $SnCl_2$ has been added. Also, in the titration of iodine solutions with $Na_2S_2O_3$, starch should not be added until just before the end point (p. 459). The color of iodine is sufficiently intense to be detected until just before the end point. Therefore $Na_2S_2O_3$ is added until the yellow color of iodine just disappears. Then starch is added and the titration completed.

Nonreversible indicators. Some dyes give a color change upon oxidation, but the change is not reversible, as it is with internal indicators. Methyl orange acts in this way in titrations with standard $KBrO_3$. Before the equivalence point, the sought-for reductant reacts more rapidly than the methyl orange with the added $KBrO_3$, reducing it to KBr. After the equivalence point, the first slight excess of $KBrO_3$ reacts with the KBr in solution to give Br_2 , which in turn bleaches the methyl orange indicator.



The action of bromine on methyl orange is irreversible, and also fairly slow. The end point must therefore be approached slowly. If the end point is overshoot, back titration is not possible. Also, the reverse titration of $KBrO_3$ with a reducing agent cannot be performed with methyl orange as an indicator. Naphthol blue-black and brilliant ponceau 5 R

dyes may be used similarly in titrations with standard KIO_3 in 4–6 M HCl solutions.

Nonreversible indicators are prone to partial oxidation by local excesses of the oxidizing agent, and therefore should not be added until just before the equivalence point. With such indicators, it is desirable to perform a first (trial) titration on a sample of the unknown, to give an estimation of the end point. Titrations on subsequent samples of the unknown may then be carried almost to the equivalence point before adding the indicator. Nonreversible indicators are no longer widely used.

20B.3. Titration of Mixtures

In principle, a mixture of two oxidants of sufficiently different strengths may be titrated potentiometrically, giving a curve with two inflection points and allowing determination of both substances. Mixtures of two reductants may be similarly determined. A substance that may be oxidized to more than one higher oxidation state may on titration give a curve with more than one inflection. In order to be distinct, the equivalence-point E 's for two successive inflection points should differ by at least 0.2 v (L12).

In practice, however, even if the E 's are well separated, the rate and reversibility are usually the greatest limitations on the titration of mixtures.

An example of the titration of a mixture of Sn(II) and Fe(II) with dichromate is described on page 473. Standard TiCl_3 and CrCl_2 (pp. 855–56) are rapidly acting reductants, and may be used to titrate mixtures of some oxidants. Other examples are given by Lingane (L12).

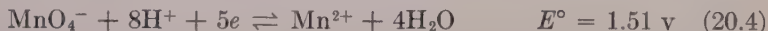
20C. PERMANGANIMETRIC TITRATIONS

KMnO_4 is a versatile and strong oxidizing agent that may be used to determine many substances by direct or indirect titration. The reactions on which these determinations are based have been well studied, and most of the determinations are highly accurate. The particular advantage of KMnO_4 is that it serves as its own indicator; because of this, it is one of the oldest, best known, and most used of standard oxidants. Recently, with the advent of internal indicators, other oxidizers are replacing KMnO_4 in certain applications. One such oxidizer is $\text{Ce(SO}_4)_2$; it is more stable than KMnO_4 and less susceptible to intermediate and side reactions.

20C.1. Classification of Permanganimetric Methods

Manganese may exist in several oxidation states, the most stable of which are 7, 6, 4, 3, and 2. The 1 and 5 oxidation states exist, but are too unstable to be of analytical interest.

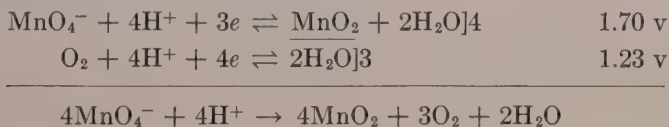
The most widely used group of permanganimetric titrations is based on the reduction of MnO_4^- to Mn^{2+} in acid solution, and only this group is discussed in this section.



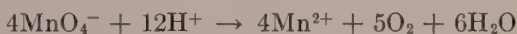
However, there are more limited titration methods that are based on the reduction of MnO_4^- to oxidation states other than Mn^{2+} ; these methods are nevertheless important, and are discussed in the Supplement (p. 837).

20C.2. Standard KMnO_4 Solutions

20C.2a. Stability. According to the TSP, KMnO_4 is unstable in water. In neutral solution the decomposition is



In acid solution the decomposition is



Fortunately, the rates of these reactions are very low, and they do not interfere in ordinary KMnO_4 titrations. However, these decompositions are catalyzed by heat, light, acid, base, and MnO_2 ; KMnO_4 solutions must therefore be prepared and used with care to prevent these decompositions from occurring.

20C.2b. Preparation and storage. For the preparation of standard solutions, reagent-grade KMnO_4 may be used without special purification. But it may not be used as a primary standard; the solutions require standardization. Ordinary standard solutions are about 0.1 *N*, but 0.01 *N* solutions may be employed in special cases.

The decomposition of KMnO_4 solutions may be negligible or extensive, depending on how they are prepared and stored (Table 20.2).

In preparing KMnO_4 solutions it is necessary to remove MnO_2 , which may be present as an impurity in the reagent KMnO_4 , or may be formed by reaction between KMnO_4 and impurities in the distilled water. Two different errors are caused if MnO_2 is not removed. (1) MnO_2 catalyzes the decomposition of KMnO_4 . (2) MnO_2 is a fairly strong

TABLE 20.2
STABILITY OF 0.05–0.10 *N* KMnO_4 SOLUTIONS*†

Experiment	Type of KMnO_4 Solution at Beginning of Experiment	Time of Treatment	Manner of Keeping	Decrease in Titer (%)
1a	Pure KMnO_4 in pure water	7 months	dark	0.2
1b			diffuse daylight	0.9
2a	Prepared by diluting pure 1 <i>N</i> KMnO_4 without filtration	7 months	dark	4.5
2b			diffuse daylight	6.0
3a	Prepared by diluting pure 1 <i>N</i> KMnO_4 and filtering through asbestos	7 months	dark	0.5
3b			diffuse daylight	1.2
4a	As in Exp. 3, with 0.02 <i>M</i> H_2SO_4	7 months	dark	9.5
4b			diffuse daylight	16.0
5a	As in Exp. 3, with 1.0 <i>M</i> H_2SO_4	7 months	dark	76
5b			diffuse daylight	95
6a	As in Exp. 3, with 0.04 <i>M</i> NaOH	7 months	dark	2.9
6b			diffuse daylight	10.5
7	Pure 0.05 <i>N</i> KMnO_4 , 0.2 <i>M</i> H_2SO_4 , heated at 100°C	1 hour	—	0.6
8	As in Exp. 7, but 0.4 <i>M</i> H_2SO_4	1 hour	—	1.7
9	As in Exp. 7, but 1.0 <i>M</i> H_2SO_4	1 hour	—	58

* Data taken from I. M. Kolthoff and I. H. Menzel, *Volumetric Analysis*, Vol. I (New York: Wiley, 1928), p. 240, with permission of the publisher.

† Relative rate of decomposition is greater in more dilute solution.

oxidizing agent in its own right, with 2 eq per mole (see TSP). Since MnO_2 is a precipitate that may not be uniformly dispersed throughout the solution, the normality of the solution may not be reproducible.

In storage and use, standard KMnO_4 should be kept away from all organic matter, which causes reduction. It is best stored in a dark, glass-stoppered bottle, since light promotes decomposition. If clear bottles are used they should be stored in a darkened locker. Even under the best storage conditions decomposition occurs slowly, and occasional restandardization is necessary. If MnO_2 forms perceptibly during storage, the solution should be decanted or filtered away from the precipitate, and then restandardized. For precise work, KMnO_4 solutions should not be heated or allowed to stand in acid or basic solutions for appreciable lengths of time. $\text{K}_2\text{Cr}_2\text{O}_7$ and $\text{Ce}(\text{SO}_4)_2$ are more stable than KMnO_4 .

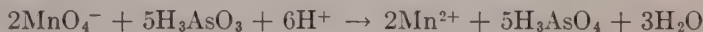
20C.2c. Standardization. There are many good primary standards for standardizing KMnO_4 solutions. As_2O_5 is discussed below, as an example of the latent errors and difficulties that are inherent even in

excellent and well-established analytical procedures. $\text{Na}_2\text{C}_2\text{O}_4$ and IK are also good primary standards (see Supplement, pp. 839–41). Fe wire is sometimes used for standardization (Exp. 20.1).

Analyzed reagent-grade As_2O_3 may be used as a primary standard without further purification. The assay value (given on the reagent bottle) usually runs well over 99.9% As_2O_3 , and the solid is easy to dry and stable in air. The solid As_2O_3 is soluble in HCl , but dissolves very slowly. For this reason, it is first dissolved in NaOH or Na_2CO_3 .



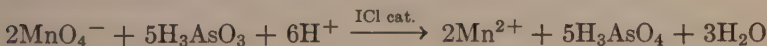
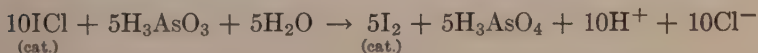
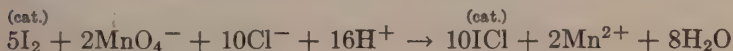
After acidification, the solution may be titrated with KMnO_4 .



There is a great tendency for H_3AsO_3 and permanganate to react in acid solution, but the uncatalyzed reaction is slow and nonstoichiometric. At room temperature much of the Mn remains in the trivalent state, which seems to be stabilized by formation of arsenate complexes. In hot HCl solution, and with slow titration, the reaction becomes more stoichiometric, but a permanent end point cannot be obtained because of the reduction of permanganate by chloride at the elevated temperature.

With a trace of iodine as a catalyst, however, the oxidation occurs rapidly, smoothly, and stoichiometrically at room temperature. Since only a trace of iodine is needed, it may be added in any valence state, and contributes insignificantly to the blank.

The mechanism of the catalysis by iodine is thought to be as follows (S36): Regardless of the original oxidation state of the trace of iodine-containing compound used, it is reduced to iodine when put into the H_3AsO_3 . The iodine is oxidized to ICl by permanganate, and the ICl in turn rapidly oxidizes H_3AsO_3 to H_3AsO_4 , becoming reduced back to iodine again, ready for a repetition of the cycle. The slow reaction between permanganate and H_3AsO_3 is thus brought about by the catalyst through two rapid steps.



Example. What is the normality of a KMnO_4 solution, 45.00 ml of which are required to titrate a 0.1500-g sample of As_2O_3 by the foregoing method?

The equivalent weight of As_2O_3 is $197.84/4$, or 49.46. Hence

$$\frac{0.1500}{49.46} \times \frac{1000}{45.00} = 0.0674 N$$

eq KMnO_4 in 1 l

— eq As_2O_3 = eq KMnO_4 in 45.00 ml

TABLE 20.3
PERMANGANIMETRIC DETERMINATIONS

A. DIRECT TITRATIONS IN ACID SOLUTION ($\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$)		
Sought-for Substance, and Its Valence Change	Method of Prereduction	Remarks
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$	Exp. 20.1	See page 476.
* $\text{Cu}^+ \rightarrow \text{Cu}^{2+}$	Ag reductor	Color interferes if Cu is too concentrated.
* $\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$	Zn	See page 455.
$\text{H}_2\text{AsO}_3 \rightarrow \text{H}_2\text{AsO}_4$	SO_2 , if necessary	Titrate with KMnO_4 , below 10°C .
$\text{H}_2\text{SbO}_3 \rightarrow \text{H}_2\text{SbO}_4$	SO_2 , if necessary	
* $\text{Ti}^{3+} \rightarrow \text{TiO}^{2+}$	Zn reductor	Air stream oxidizes U(III) to U(IV).
$\text{U}^{4+} \rightarrow \text{UO}_2^{2+}$	Zn reductor gives U(III, IV)	
$\text{VO}^{2+} \rightarrow \text{VO}_3^+$	SO_2 or H_2S	
* $\text{V}^{2+} \rightarrow \text{VO}_2^+$	Zn reductor	
$\text{W}^{3+} \rightarrow \text{WO}_4^-$	Pb amalgam at 50°C , conc. HCl	
* $\text{Mo}^{3+} \rightarrow \text{MoO}_4^-$	Zn reductor	
† $\text{HNO}_2 \rightarrow \text{HNO}_3$		
$\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{CN})_6^{3-}$		
$\text{H}_2\text{O}_2 \rightarrow \text{O}_2$		See page 839.
$\text{H}_2\text{C}_2\text{O}_4 \rightarrow \text{CO}_2$		See page 840.
$\text{I}^- \rightarrow \text{ICl}$		
† $\text{SeO}_3^- \rightarrow \text{SeO}_4^-$		
† $\text{TeO}_3^- \rightarrow \text{TeO}_4^-$		
B. INDIRECT TITRATIONS IN ACID SOLUTION ($\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$)		
Sought-for Substance, and Its Valence Change	Remarks	
† $\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$	Preoxidation with NaBiO_3 , PbO_3 , or $(\text{NH}_4)_2\text{S}_2\text{O}_8$.	
† $\text{MnO}_2 \rightarrow \text{Mn}^{2+}$	Preoxidation with KClO_3 in conc. HNO_3 . MnO_2 filtered off. Ford-Williams method.	
† $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$	Preoxidation with NaBiO_3 or $(\text{NH}_4)_2\text{S}_2\text{O}_8$.	
† $\text{Cr}_2\text{O}_7^- \rightarrow \text{Cr}^{3+}$		
† $\text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-}$		
Ba^{2+} , Pb^{2+}	Precipitate chromates. Filter, wash, dissolve in acid solution, and determine Cr_2O_7^- as above.	
Ca^{2+} , Sr^{2+} , Ba^{2+} }.....	Precipitate as oxalates. Filter, wash, dissolve in H_2SO_4 , and determine $\text{H}_2\text{C}_2\text{O}_4$ as in Table A.	
Zn^{2+} , Pb^{2+} , Hg_2^{2+} }.....	Precipitate $\text{K}_3\text{Co}(\text{NO}_2)_6$. Wash sparingly, dissolve in acid, and determine HNO_2 as in Table A. $\text{K}_3\text{Co}(\text{NO}_2)_6$ shows only 11 eq/mole, since Co^{3+} is reduced to Co^{2+} in the acid permanganate solution.	
Ce^{3+} , La^{3+} , BiO^+ }.....	Precipitate $\text{NaZn}(\text{UO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_9 \cdot 6\text{H}_2\text{O}$. Wash sparingly, dissolve in dilute H_2SO_4 , and determine UO_2^{2+} as in Table A.	
Na^+	Precipitate $(\text{NH}_4)_2\text{PO}_4 \cdot 12\text{MoO}_3$. Wash, dissolve in NH_3 , acidify with H_2SO_4 , and determine Mo as in Table A.	
PO_4^{3-}		

*To diminish error due to air-oxidation after prereduction and during titration, the prereduced forms are sometimes added to an (unmeasured) excess of ferric alum. The equivalent amount of Fe(II) formed is not rapidly oxidizable by air, and may be titrated directly with standard KMnO_4 .

†Direct titration is slow and/or inaccurate. Accepted procedure is to add excess standard KMnO_4 , and then to back-titrate the excess KMnO_4 with standard FeSO_4 or other reducing agent.

‡A measured excess of a standard reducing solution is added, usually standard FeSO_4 , but sometimes $\text{H}_2\text{C}_2\text{O}_4$ or H_2AsO_3 . After reaction, the remaining excess of reductant is determined by titration with standard KMnO_4 .

20C.3. Permanganimetric Determinations

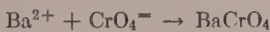
A large number of reducing agents may be determined directly by titration with standard KMnO_4 (Table 20.3A), and many oxidizing agents may be determined indirectly (Table 20.3B).

Even substances that are neither oxidizers nor reducers may be determined, by causing them to react stoichiometrically with a substance that can be titrated with permanganate, as outlined in the following example and in Table 20.3B.

Only a small excess (about $2 \times 10^{-6} M$) of KMnO_4 need be added past the equivalence point to establish the end-point pink coloration. The blank is therefore small when 0.1 N KMnO_4 solutions are used. However, for more dilute solutions (i.e., 0.01 N), the blank is significant, and the use of a more sensitive internal redox indicator is recommended. To prevent irreversible oxidation of the indicator by local excesses of KMnO_4 before the equivalence point is reached, it may be desirable to withhold the indicator until just before the equivalence point.

Example. A 2.000-g sample containing BaCl_2 and NaCl is dissolved, and the Ba is precipitated as BaCrO_4 . The washed precipitate is dissolved in HCl , and 50.00 ml of 0.1000 N FeSO_4 are added. The excess Fe(II) requires 6.35 ml of 0.1500 N KMnO_4 for titration. What is the % BaCl_2 in the sample?

The equations for the reactions are:



From these equations, it may be seen that

$$1 \text{ mole } \text{BaCl}_2 = 1 \text{ mole } \text{CrO}_4^{=} = \frac{1}{2} \text{ mole } \text{Cr}_2\text{O}_7^{=}, \text{ or } \frac{1}{2} \times 6 \text{ eq}$$

Hence the equivalent weight of BaCl_2 is 208.25/3, or 69.42. (After some experience is gained, it is not necessary to write the balanced chemical equations to find the equivalent weight of the sought-for substance.)

$$\begin{aligned} \left(\begin{array}{c} \text{meq dichromate,} \\ \text{or meq } \text{BaCl}_2 \end{array} \right) &= \left(\begin{array}{c} \text{total meq} \\ \text{FeSO}_4 \text{ added} \end{array} \right) - \left(\begin{array}{c} \text{meq of } \text{KMnO}_4 \text{ used} \\ \text{in back titration} \end{array} \right) \\ &= 0.1000 (50.00) - 0.1500 (6.35) = 4.048 \end{aligned}$$

$$\begin{array}{c} 4.048 \left| \begin{array}{l} \times 69.42 \\ \times \frac{100}{2000} \end{array} \right| = 14.05\% \text{ BaCl}_2 \\ \left| \begin{array}{l} \text{mg BaCl}_2 \\ \text{meq dichromate, or meq BaCl}_2 \end{array} \right| \end{array}$$

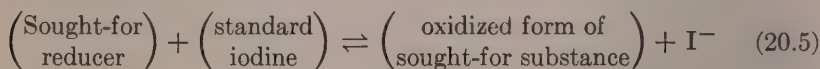
20D. IODIMETRIC TITRATIONS

20D.1. Classification of Iodimetric Methods

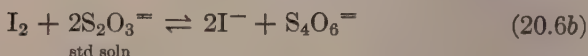
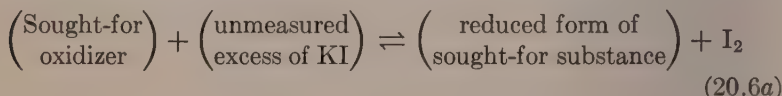
There are many titrations that are based on reactions involving iodine. In this section, only *iodimetric* titrations are discussed—that is, ones based on the iodine-iodide half-reaction. Titrations based on higher oxidation states of iodine are outlined in the Supplement (p. 842).

The unique property of the iodine-iodide half-reaction, as compared to others involving standard oxidants or reductants, is its intermediate position in the TSP (0.54 v). This intermediate potential allows determination of both oxidizing and reducing agents.

Standard iodine solutions may be used to titrate fairly strong reducers directly.



On the other hand, KI may be used in conjunction with standard $\text{Na}_2\text{S}_2\text{O}_3$ to determine fairly strong oxidizers indirectly.



Even though the method is indirect, only one standard solution is required. Even substances which react incompletely with KI may be quantitatively determined, for iodine is removed in the titration, forcing equilibrium 20.6a to the right.

There are further reasons for the prevalence of iodimetric methods. Starch is an excellent visual indicator, as is also the color of iodine in chloroform. Also, $\text{Na}_2\text{S}_2\text{O}_3$ solutions are more stable than most other standard reducing solutions.

20D.2. Establishing the Equivalence Point in Iodimetric Methods

20D.2a. The starch end point. Starch forms an intense blue compound with traces of iodine. Water and iodide are also involved in the complex, which is really a hydrated colloidal particle with iodide and iodine adsorbed upon it. The blue color is readily reversible, and may be used as a sensitive indicator for traces of iodine in solution.



Iodine in concentrations as low as $10^{-7} M$ may be detected, provided that the concentration of iodide is $10^{-4} M$ or greater. If $[I^-]$ is lower than $10^{-4} M$, the test is less sensitive (S36).

Since the blue color is destroyed by alkalis, titrations to a starch end point should be made below pH 8. In general, agents that coagulate colloids or hinder adsorption of iodine decrease the sensitivity of the test. Titrations to a starch end point should never be made in warm solutions. Alcohol and concentrated solutions of strong electrolytes should be avoided if possible.

Most frequently, iodine solutions are titrated with standard $Na_2S_2O_3$ to the disappearance of the blue color at the end point. In such titrations, the starch indicator should not be added until just before the end point, when the iodine concentration is low. If it is added too early in the titration, undesirable reactions occur. In acid solutions, starch hydrolyzes to products that give a nonreversible reddish color with iodine, and mask the true end-point change. Iodine accelerates this hydrolysis. In practice, therefore, the starch indicator is withheld until the last tinge of yellow due to excess iodine disappears; starch is then added and the titration is quickly completed.

The starch end point is such an excellent one that it is used in the great majority of all iodimetric titrations.

Actually, only one component (α -amylose) of ordinary starch gives the blue color with iodine. This component is available as *soluble starch*, which dissolves readily in water. The α -amylose is extracted from ordinary starches by making the starch into a paste, grinding, diluting, boiling to break up the granules, letting the insoluble portion (β -amylose) settle, and then decanting the portion containing the soluble α -amylose. The β -amylose forms a reddish color with iodine, but the reaction is much less reversible than for α -amylose. Not all starches are suitable for indicator preparation, since some (like corn-starch) contain a high proportion of β -amylose. Potato, rice, or arrow-root starches are most frequently used to prepare soluble starch.

Unpreserved starch solutions become moldy in a few days, and bacterial action gives detrimental products similar to those of hydrolysis. Preservatives (HgI_2 , boric acid, or furoic acid) may be added to prevent molds. Alternatively, starch solutions should be prepared fresh every few days. Starch in formamide solution is said to be very stable (H9).

20D.2b. The extraction end point. Iodine gives very intensely colored purple solutions in chloroform ($CHCl_3$) or carbon tetrachloride (CCl_4), solvents that are immiscible with water. Very low concentrations of iodine in large volumes of aqueous solution may be determined by adding a relatively small volume of CCl_4 and shaking to extract the iodine

from the aqueous into the CCl_4 layer. When this method is used to establish an end point, the titration is carried out in a glass-stoppered Erlenmeyer flask. A few milliliters of CCl_4 are added, and the stoppered flask is shaken and inverted, so that the heavy CCl_4 settles into the narrow neck of the flask, where its color may be examined. Titrations may be made either to the appearance or disappearance of the purple iodine color. Less than 0.01 ml of 0.1 *N* iodine is required to give a perceptible color to a system containing 200 ml of 1 *M* HCl and 10 ml of CCl_4 . The extraction method is as sensitive as the starch method, but requires more time, for the system must be stoppered, shaken, allowed to settle, and examined after each portion of standard solution is added. The extraction method is used principally for titrations in strongly acid solution, where starch is inapplicable.

20D.2c. Potentiometric titrations. Iodimetric titrations are seldom performed potentiometrically because (1) visual end points are very satisfactory and require less time, and (2) it is more difficult to exclude error due to air-oxidation. With proper precautions, however, potentiometric titrations may be made very accurately with a bright Pt electrode, which is reversible for the iodine-iodide half-reaction.

20D.3. Direct Titrations with Standard Iodine

20D.3a. Standard iodine solutions

Preparation. Analyzed reagent-grade iodine is suitable without further purification for use as a primary standard. Because of the corrosiveness and volatility of iodine, the preparation of solutions from iodine as a primary standard is not always recommended; instead the solutions are prepared approximately and then standardized with As_2O_3 or $\text{Na}_2\text{S}_2\text{O}_3$.

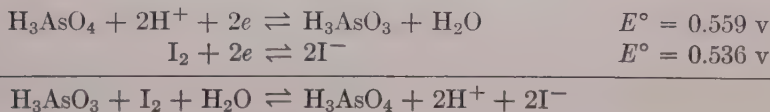
The solubility of iodine in water is only 0.00134 *M* at 25°C, and is not sufficiently high for preparation of 0.1 *N* standard solutions. However, the solubility of iodine is increased by the presence of KI.



Hence by making the solution about 0.1 *M* in KI, the solution may easily be brought up to 0.05 *M* in I_3^- , or 0.1 *N* in oxidizing strength. It should be noted that iodine exists predominantly as I_3^- (not as I_2) in solutions containing moderate concentrations of iodide.*

*In describing the state of iodine in iodide solutions, it would be more exact to represent iodine as I_3^- . For greater ease in perceiving stoichiometrical relationships, however, it seems more direct to represent iodine as I_2 in chemical equations, and this procedure will be followed in this chapter. Thus although the symbol I_2 is used, the reader should understand that in many instances the iodine is predominantly in the form of I_3^- . In the quantitative treatment of equilibria, it is very important to distinguish whether iodine exists predominantly as I_2 or as I_3^- in the system.

Standardization. Iodine solutions are often standardized against standard $\text{Na}_2\text{S}_2\text{O}_3$ solutions. The only widely used primary standard is As_2O_3 . Under the proper conditions, the reaction with iodine is



This reaction aptly illustrates the effect of $p\text{H}$ upon the completeness of a redox reaction. From the magnitude of the standard potentials, the iodine- H_3AsO_3 reaction should be incomplete. By the proper selection of conditions, however, this reaction may be made to proceed quantitatively in either direction.

In order that the direct titration of H_3AsO_3 with standard iodine may proceed quantitatively, it is necessary to perform the titration at low acidity. The $p\text{H}$ must fall above 4 for complete reaction (see Supplement, p. 849). Also, the reaction mixture must be buffered, otherwise the H^+ produced by the reaction might build up sufficiently to prevent complete reaction. Actually, the $p\text{H}$ may be between 4 and 9, with 7 being optimum. (Above $p\text{H}$ 9 the disproportionation of iodine becomes appreciable. Below $p\text{H}$ 7 the rate of reaction falls off.)

Another way of making the I_2 - H_3AsO_3 reaction proceed quantitatively is to carry out the titration in the presence of HgCl_2 , which binds I^- into a very stable complex, and which greatly increases the oxidizing power of iodine. The HgCl_2 interferes with the starch indicator, so the extraction method is used to establish the end point.

At high acidity, the reverse reaction is the basis for an indirect determination of As. Arsenic is preoxidized quantitatively to H_3AsO_4 , and an excess of KI is added. The iodine formed is then titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$. Removal of iodine by titration also helps to drive the reaction to the left.

Example. What is the normality of an iodine solution, 37.26 ml of which are required to titrate a 0.5000-g sample of As_2O_3 by the foregoing method?

$1\text{As}_2\text{O}_3 = 2\text{H}_3\text{AsO}_3 = 4 \text{ eq.}$ The equivalent weight of As_2O_3 is $197.84/4$, or 49.46.

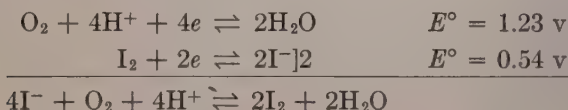
$$\left. \begin{array}{l} \frac{0.5000}{49.46} \times \frac{1000}{37.26} = 0.2714 \text{ N} \\ \text{eq As}_2\text{O}_3 = \text{eq iodine in 37.26 ml} \end{array} \right\} \begin{array}{l} \text{eq iodine in 1 l} \end{array}$$

20D.3b. Sources of error in titrations with standard iodine. Since they are unstable in several respects, standard iodine solutions must be stored and used with several precautions, and must be restandardized daily.

1. Iodine solutions attack rubber and most organic materials; they should be stored in glass-stoppered bottles, out of contact with rubber, dust, and reducing gases such as SO_2 and H_2S .

2. The vapor pressure of iodine is appreciable over 0.10 M KI –0.05 M I_2 solutions, and iodine is slowly lost unless the system is kept closed during storage. During the short time required for an ordinary titration, volatilization is negligible and no special precautions need be taken to prevent loss.

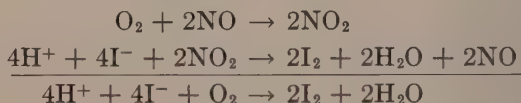
3. Iodide is oxidizable by air.



Fortunately, this reaction is slow in neutral solution, and causes no appreciable error in titrations performed in neutral solutions. However, the rate increases with acid concentration. When iodimetric titrations must be performed in acid solutions, air must be excluded, and the titrations should be performed quickly.

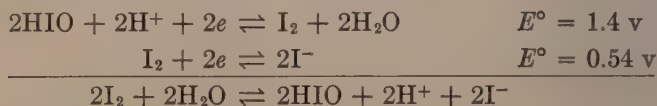
The oxidation is accelerated by light and heat; therefore standard iodine solutions should be kept in a darkened locker and should never be warmed.

The air-oxidation of I^- may be catalyzed or induced by a variety of substances, and may cause error in both direct and indirect titrations. Typical examples of catalysts are nitrogen oxides or Cu^{2+} , a simplified mechanism for NO or NO_2 being

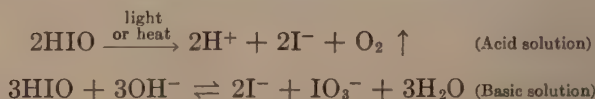


On the other hand, the reaction of I^- with $\text{S}_2\text{O}_8^{=}$, Fe^{3+} , $\text{Fe}(\text{CN})_6^{=}$, or $\text{V}(\text{V})$ induces the air-oxidation of I^- . The mechanism of induction by the I^- - $\text{V}(\text{V})$ reaction is summarized by Laitinen (12, p. 467).

4. Iodine may undergo disproportionation.



In turn, HIO may decompose further in two ways,

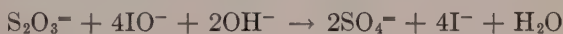


In acid solution, $[\text{HIO}]$ is so low that the rate of decomposition is inappreciable. In basic solutions, however, the equilibria lie preponderantly to the right. To keep error due to these reactions negligible in iodimetric methods, the pH must be kept below 9.

20D.4. Indirect Titrations with Thiosulfate

20D.4a. Titration conditions. The basis of all indirect iodimetric methods is the titration of iodine with standard $\text{Na}_2\text{S}_2\text{O}_3$ (Eq. 20.6b). The reaction proceeds rapidly, smoothly, and stoichiometrically at pH 5–9. The same is true of the reverse titration of $\text{Na}_2\text{S}_2\text{O}_3$ with iodine, but this is seldom done. The mechanism of the reaction is given in the Supplement (p. 850).

Above pH 9 there is not only error due to disproportionation of iodine, but the HIO formed is a strong oxidizing agent that slowly oxidizes thiosulfate to sulfate.



Below pH 5 iodine solutions may be titrated with $\text{Na}_2\text{S}_2\text{O}_3$, but care must be used to prevent the air-oxidation of iodide. The acid decomposition of $\text{Na}_2\text{S}_2\text{O}_3$ is negligible, provided that the standard $\text{Na}_2\text{S}_2\text{O}_3$ is added with good stirring to ensure that local excesses of $\text{Na}_2\text{S}_2\text{O}_3$ do not occur; if stirred well, the thiosulfate reacts with the iodine so rapidly that there is no opportunity for the slower decomposition reaction to occur. With suitable precautions to prevent air-oxidation and decomposition, titration of iodine in 3–4 N acid solutions may be safely made with 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.

If an iodine solution is titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$ containing Na_2CO_3 or $\text{Na}_2\text{B}_4\text{O}_7$ as a preservative, the iodine solution should be acidified or buffered at a proper pH ; otherwise it may become too basic before the end point is reached.

Example. What is the normality of an iodine solution, 25.00 ml of which require 30.25 ml of 0.1000 N $\text{Na}_2\text{S}_2\text{O}_3$ for titration? Give the equivalent weights of iodine and $\text{Na}_2\text{S}_2\text{O}_3$.

$$0.1000 \times 30.25 / 25.00 = 0.1210 N$$

— meq iodine in 1 ml

— meq $\text{Na}_2\text{S}_2\text{O}_3$ = meq iodine in 25.00 ml

There are 2 eq per mole of I_2 , since $\text{I}_2 + 2e \rightleftharpoons 2\text{I}^-$. The equivalent weight of iodine is therefore $2 \times 126.91/2$, or 126.91.

There is 1 eq per mole of $\text{Na}_2\text{S}_2\text{O}_3$, since $\text{S}_4\text{O}_6^{2-} + 2e \rightleftharpoons 2\text{S}_2\text{O}_3^{2-}$. The equivalent weight is therefore the same as the molecular weight, 158.11.

20D.4b. Standard $\text{Na}_2\text{S}_2\text{O}_3$ solution

Preparation and storage. Although standard $\text{Na}_2\text{S}_2\text{O}_3$ solution is more stable than most other standard reducing solutions, it should be used and stored with precautions, and should be restandardized occasionally.

1. Bacterial action is the major cause of decomposition of $\text{Na}_2\text{S}_2\text{O}_3$ during storage. To reduce such decomposition, boiled (sterile) water is used to prepare the solution. Preservatives also may be used, provided that they do not interfere in the titrations to be made. Borax and Na_2CO_3 , which hydrolyze to pH 8–9, inhibit the bacterial action. Mercury salts— HgI_2 , $\text{Hg}(\text{CN})_2$ —are bactericidal, and are favored over Na_2CO_3 or borax because they do not make the solution alkaline. Unpreserved 0.1 N solutions decrease in titer by about 10% in 6 months under ordinary storage conditions, whereas solutions preserved with Na_2CO_3 or borax decrease only 1–2%. Dilute solutions decompose relatively faster than concentrated ones.

2. $\text{Na}_2\text{S}_2\text{O}_3$ decomposes in acid solutions.



This decomposition is accelerated by light, and $\text{Na}_2\text{S}_2\text{O}_3$ solutions should be kept in a darkened locker when not in use. Cloudy $\text{Na}_2\text{S}_2\text{O}_3$ solutions should be rejected. The rate of this decomposition is low, and it is usually not significant in neutral or slightly alkaline solutions. Standard $\text{Na}_2\text{S}_2\text{O}_3$ solutions should never be acidified.

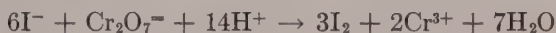
3. $\text{Na}_2\text{S}_2\text{O}_3$ is subject to air-oxidation. A mixture of products is formed, including tetrathionate ($\text{S}_4\text{O}_6^{2-}$), sulfite, and sulfate, the proportions of each being dependent upon pH and time of oxidation. Fortunately, the rate of oxidation is so low that standard $\text{Na}_2\text{S}_2\text{O}_3$ solution saturated with oxygen does not change significantly in titer during storage. Acid increases the rate of oxidation. Some substances, such as $\text{Cu}(\text{II})$, catalyze the oxidation.

Standardization. Anhydrous reagent-grade $\text{Na}_2\text{S}_2\text{O}_3$ may be easily dried and used as a primary standard for preparing $\text{Na}_2\text{S}_2\text{O}_3$ solutions (v4). $\text{BaS}_2\text{O}_3 \cdot \text{H}_2\text{O}$ may also be used. However, the usual procedure is to prepare a solution of approximately the desired normality, and then to standardize in any of several ways.

There are many excellent primary standard substances for standardizing $\text{Na}_2\text{S}_2\text{O}_3$ solutions. The more common ones are iodine, $\text{K}_2\text{Cr}_2\text{O}_7$, KIO_3 , and electrolytic Cu . Others are CuO , KBrO_3 , and $\text{K}_3\text{Fe}(\text{CN})_6$. Standard KMnO_4 or $\text{Ce}(\text{SO}_4)_2$ solutions are often used because of their availability. The iodine-thiosulfate reaction is discussed on page 463. The standardization with Cu is given in Exp. 20.3 (p. 488). The use of $\text{K}_3\text{Fe}(\text{CN})_6$ is described in the Supplement (p. 850).

The indirect standardization of $\text{Na}_2\text{S}_2\text{O}_3$ with $\text{K}_2\text{Cr}_2\text{O}_7$ is described here because the reaction is typical of the indirect titration of many strong oxidizing agents, such as KIO_3 , KBrO_3 , KMnO_4 , and $\text{Ce}(\text{SO}_4)_2$. Generally, oxidizing agents react neither rapidly nor stoichiometrically with $\text{Na}_2\text{S}_2\text{O}_3$ in acid solution. Some of the oxidation states produced are free sulfur, $\text{S}_2\text{O}_6^{=}$ (dithionate), $\text{S}_4\text{O}_6^{=}$, and $\text{SO}_4^{=}$. Direct titration of an oxidant like $\text{K}_2\text{Cr}_2\text{O}_7$ in acid solution is therefore not possible, and the following indirect method is used.

Excesses of HCl and KI are added to a known amount of primary standard $\text{K}_2\text{Cr}_2\text{O}_7$. The reaction is not rapid, so a few minutes are allowed for completion.



The iodine formed is then titrated with the $\text{Na}_2\text{S}_2\text{O}_3$ to be standardized, using starch indicator. A fairly high excess of acid must be used in order to make the reaction proceed rapidly and to completion. This excess acid cannot be neutralized before the $\text{Na}_2\text{S}_2\text{O}_3$ titration, for gray-green hydrous $\text{Cr}(\text{OH})_3$ would precipitate, obscuring the end point. For this reason, titration with $\text{Na}_2\text{S}_2\text{O}_3$ must be made in an acid medium.

It has been shown that the $\text{Cr}(\text{III})$ formed catalyzes the air-oxidation of I^- , causing a fading end point. Tartaric acid complexes $\text{Cr}(\text{III})$ and inhibits the catalysis, giving an acceptable end point (v3). Another way of preventing the air-oxidation of I^- is to pass a stream of CO_2 through the solution before and during titration. Or, NaHCO_3 may be added to the flask after the $\text{Cr}_2\text{O}_7^{=}\text{-I}^-$ reaction is complete. The NaHCO_3 reacts with a part of the excess acid, forming CO_2 , which sweeps air out of the flask and solution.

A blank must be determined because the large amount of KI used may contain a significant amount of KIO_3 as an impurity, which reacts with KI in acid solution to give iodine.



The blank may also be contributed to by air-oxidation of the iodide.

Example 1. After addition of excess acid and KI , a 0.5000-g sample of $\text{K}_2\text{Cr}_2\text{O}_7$ requires 39.82 ml of an $\text{Na}_2\text{S}_2\text{O}_3$ solution for titration. What is the normality of the $\text{Na}_2\text{S}_2\text{O}_3$?

The equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ is 294.19/6, or 49.032.

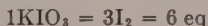
$$\frac{0.5000}{49.032} \times \frac{1000}{39.82} = 0.2561 N$$

eq $\text{Na}_2\text{S}_2\text{O}_3$ per liter

eq $\text{K}_2\text{Cr}_2\text{O}_7$ = eq $\text{Na}_2\text{S}_2\text{O}_3$ in 39.82 ml

Example 2. After addition of excess acid and KI, a 0.2000-g sample of KIO_3 requires 40.72 ml of $\text{Na}_2\text{S}_2\text{O}_3$ for titration. What is the normality of the $\text{Na}_2\text{S}_2\text{O}_3$? (The reaction is given above.)

It is easy to use the incorrect equivalent weight of KIO_3 in this problem. It does not suffice to reason that there are 5 eq per mole of KIO_3 because the oxidation number of I changes from +5 to 0. This reasoning is correct, but it does not go far enough. It must be recognized that not all of the iodine which is liberated (and later titrated by the $\text{Na}_2\text{S}_2\text{O}_3$) comes from the KI alone, but that some of the iodine comes from the oxidizing agent itself. Actually, 1 mole of KIO_3 yields 3 moles of I_2 , or 6 equivalents.



Hence the equivalent weight of KIO_3 is 214.00/6, or 35.667.

$$\frac{0.2000}{35.667} \times \frac{1000}{40.72} = 0.1377 N$$

eq $\text{Na}_2\text{S}_2\text{O}_3$ per liter

eq KIO_3 = eq $\text{Na}_2\text{S}_2\text{O}_3$ in 40.72 ml

20D.5. Iodimetric Determinations

A large number of substances may be determined directly or indirectly by iodimetric methods. Some of these methods are outlined in Table 20.4.

Example 1. What is the molarity of a solution of hydrazine sulfate, 25.00 ml of which require 27.29 ml of 0.1000 N iodine for titration?

$$0.1000 \times \frac{27.29}{25.00} = 0.1092 N \text{ N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$$

Hydrazine possesses 4 eq per mole on reaction with iodine (Table 20.4A). Hence the molarity is 0.1092/4, or 0.02730 M .

Example 2. A 1.000-g sample of a Zn ore is dissolved and the Zn is quantitatively recovered as ZnS , after removal of interferences. The precipitate is added to 50.00 ml of a 0.1000 N iodine solution containing 50 ml of 0.1 M H_2SO_4 , care being taken to exclude air. After reaction is complete, titration of the excess iodine requires 3.26 ml of 0.1153 N $\text{Na}_2\text{S}_2\text{O}_3$. Calculate the Zn content of the ore as % ZnO .

$$\left(\begin{array}{l} \text{meq of iodine} \\ \text{reacting with the} \\ \text{sulfide from ZnS} \end{array} \right) = \begin{array}{c} \text{Meq iodine added.} \\ \text{Meq excess iodine titrated with Na}_2\text{S}_2\text{O}_3. \end{array} = (0.1000 \times 50.00) - (0.1153 \times 3.26) = 4.624$$



$$4.624 \times \frac{81.37}{2} \times \frac{100}{1000} = 18.82\% \text{ ZnO}$$

mg ZnO

meq iodine = meq ZnO

TABLE 20.4

IODIMETRIC DETERMINATIONS

A. DIRECT TITRATIONS (WITH STANDARD IODINE)*

Sought-for Substance and Its Valence Change	Remarks
$\text{H}_3\text{AsO}_3 \rightarrow \text{H}_3\text{AsO}_4$	See page 461.
$\text{H}_3\text{SbO}_3 \rightarrow \text{H}_3\text{SbO}_4$	} Neutral or very weakly acid solution.
$\text{VO}^{2+} \rightarrow \text{VO}_2^+$	
$\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{CN})_6^{3-}$	Prereducer with SO_2 .
$\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-}$	See page 463.
$\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$	Prereducer with Zn, Pb, Sb, etc.
$\text{H}_2\text{S} \rightarrow \text{S}$	} Tendency toward loss by volatilization in acid solution.†
$\text{H}_2\text{SO}_3 \rightarrow \text{H}_2\text{SO}_4$	
$\text{H}_3\text{PO}_3 \rightarrow \text{H}_3\text{PO}_4$	Slow reaction.† H_3PO_2 does not interfere in neutral solution.
$\text{H}_3\text{PO}_3 \rightarrow \text{H}_3\text{PO}_4$	Slow reaction.† H_3PO_3 does not interfere in 1.5 M HCl.
$\text{H}_2\text{PO}_3 \rightarrow \text{H}_2\text{PO}_4$	} Neutral or weakly alkaline solution.
$2\text{NH}_4\text{OH} \cdot \text{HCl} \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O} + 6\text{H}^+ + 2\text{Cl}^- + 4\text{e}^-$	
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 \rightarrow \text{N}_2 + \text{SO}_4^{2-} + 6\text{H}^+ + 4\text{e}^-$	In NaHCO_3 buffered solution.
Unsaturation in organic compounds	
$\text{C}=\text{C} + \text{I}_2 \rightarrow \text{CI}-\text{CI}$	Determination of iodine number of fats and oils.‡

B. INDIRECT TITRATIONS (WITH STANDARD $\text{Na}_2\text{S}_2\text{O}_3$)§

$\text{MnO}_4^- \rightarrow \text{Mn}^{2+}$	See page 465.
$\text{Cr}_2\text{O}_7^{2-} \rightarrow \text{Cr}^{3+}$	
$\text{O}_3 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}$	Above pH 7, O_3 may be determined in the presence of O_2 .
$\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightleftharpoons 2\text{H}_2\text{O}$	See page 845.
$\text{IO}_3^- \rightarrow \text{I}^-$	
$\text{BrO}_3^- \rightarrow \text{Br}^-$	Also other oxyhalogen acids.
$\text{ClO}_3^- \rightarrow \text{Cl}^-$	
$\text{IO}_4^- \rightarrow \text{I}^-$	Exp. 20.3 (p. 488).
$\text{HClO} \rightarrow \text{Cl}^-$	
$\text{HNO}_2 \rightarrow \text{NO}$	Also bromine.
$\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$	Direct titration.
$\text{Cu}^{2+} \rightarrow \text{CuI}$	CuI catalyst.
$\text{Cl}_2 \rightarrow \text{Cl}^-$	See page 850.
$\text{I}_2 \rightarrow \text{I}^-$	See page 461.
$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	
$\text{Fe}(\text{CN})_6^{3-} \rightarrow \text{Fe}(\text{CN})_6^{4-}$	
$\text{H}_3\text{AsO}_4 \rightarrow \text{H}_3\text{AsO}_3$	
$\text{H}_3\text{SbO}_4 \rightarrow \text{H}_3\text{SbO}_3$	

C. OTHER INDIRECT METHODS

$\text{Pb}^{2+}, \text{Ba}^{2+}$	Precipitate chromates. Filter, wash, dissolve in acid solution, and determine $\text{Cr}_2\text{O}_7^{2-}$ as in Table B.
MnO_2	Treat with conc. HCl, and determine Cl_2 as in Table B.
I^-	$\text{MnO}_2 + 4\text{HCl} \rightarrow \text{MnCl}_2 + \text{H}_2\text{O} + \text{Cl}_2$
$\text{Zn}^{2+}, \text{Cd}^{2+}$, also other metals forming insoluble sulfides	Oxidize with excess bromine to IO_3^- , which is determined as in Table B.
H^+	Precipitate and wash insoluble sulfide. Dissolve sulfide in acid solution containing a measured excess of standard iodine, and back-titrate with standard $\text{Na}_2\text{S}_2\text{O}_3$.
$\text{R}-\text{CHO} + \text{HSO}_3^- \rightarrow \text{R}-\underset{\text{OH}}{\text{CH}}-\text{SO}_3^-$	See page 845.
aldehyde	Add a measured excess of standard NaHSO_3 , and titrate excess as in Table A, after formation of addition compound is complete.‡

*Sought-for substance titrated with standard iodine in acid solution, unless noted otherwise.

†Add a measured excess of standard iodine, and back-titrate with standard thiosulfate or arsenite.

‡Iodimetric methods of determining other kinds of organic compounds are described in other texts

(F11, S14).

§Add excess KI to acid solution of sought-for oxidant. Titrate iodine formed with standard $\text{Na}_2\text{S}_2\text{O}_3$.

20E. CERATE TITRATIONS

20E.1. Properties of Cerate Solutions

20E.1a. Oxidizing power. Cerate shows a rather complicated behavior in aqueous solution. It forms anionic complexes, such as $\text{Ce}(\text{SO}_4)_3^-$, CeCl_6^- , and $\text{Ce}(\text{NO}_3)_6^-$. Furthermore, Ce(IV) is strongly hydrolyzed, and appears to exist largely as $\text{Ce}(\text{OH})^{3+}$ and $\text{Ce}(\text{OH})_2^{2+}$ in solutions of moderate acidity (S13). Ce^{4+} probably exists appreciably only in solutions of very high acidity. As a result, the oxidizing power of Ce(IV) depends largely upon the nature and concentration of the acid present. Formal E 's of 0.025 M Ce(IV) and 0.025 M Ce(III) in various acids are

$$1.87 \text{ v (8 } M \text{ HClO}_4\text{)} \quad 1.61 \text{ v (1 } M \text{ HNO}_3\text{)}$$

$$1.70 \text{ v (1 } M \text{ HClO}_4\text{)} \quad 1.44 \text{ v (1 } M \text{ H}_2\text{SO}_4\text{)}$$

Cerate is therefore a highly versatile oxidizing agent, whose strength may be adjusted over a considerable range simply by altering the composition of the system in which the cerate is used.

20E.1b. Preparation and stability. The Ce(IV) compounds most available are ceric hydroxide, $\text{Ce}(\text{OH})_4$, ammonium sulfatocerate, $2(\text{NH}_4)_2\text{SO}_4 \cdot \text{Ce}(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$, and ammonium hexanitratocerate, $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$. None of these is a good primary standard. The salts are difficult to dissolve, and the hydroxide contains indeterminate amounts of water. Cerate solutions are therefore made up approximately and then standardized.

Standard solutions of 0.1 M $\text{Ce}(\text{SO}_4)_2$ in 1 M H_2SO_4 are stable for years at 25°C, and may even be heated to 100°C for considerable lengths of time without appreciable change in titer. The standard solution in 1 M H_2SO_4 is preferred as a titrant. In HNO_3 or HClO_4 , ammonium sulfatocerate or hexanitratocerate decreases 0.3–0.7% in titer over periods of 15–30 days in the dark. The decomposition is accelerated by light. Cerate is not stable in HCl solutions, chloride being slowly oxidized to chlorine. However, this oxidation is slow, and reducers may be accurately titrated with cerate in the presence of chloride.

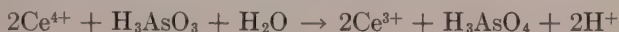
20E.1c. Cerate compared with KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$. Standard cerate combines the advantages of both standard KMnO_4 and $\text{K}_2\text{Cr}_2\text{O}_7$ solutions, and is therefore superseding them in many applications. (1) The oxidizing strength of cerate is easily variable. Cerate has an oxidizing strength comparable to that of $\text{K}_2\text{Cr}_2\text{O}_7$, if titrations are performed in H_2SO_4 solution. Cerate in H_2SO_4 is a better titrant than KMnO_4 for the determination of Fe(II) in the presence of chloride, since chloride is not oxidized. On the other hand, if titrations are made in HClO_4 solution, cerate is a considerably stronger oxidant than KMnO_4 . (2) There

exist a number of indicators with high transition potentials, which transit in rather strongly oxidizing solutions. Ferroin is excellent for cerate titrations in HCl or H₂SO₄ solutions; for titrations in HNO₃ or HClO₄ solutions, nitroferroin often suffices. These indicators give sharp and reversible color changes. The potentiometric method of establishing the end point also works well in cerate titrations. (3) Standard cerate solutions are more stable than KMnO₄ solutions of the same normality. (4) Since Ce has only two oxidation states, the possibility of induced and side reactions is less than for KMnO₄ solutions. (5) While the color of 0.1 *N* cerate solution is an intense yellow, there is no interference with the reading of the meniscus, as with 0.1 *N* KMnO₄. Also, Ce(III) is practically colorless, while Cr(III), the reduction product of K₂Cr₂O₇, is green; thus Ce(III) allows more effective use of indicators. (6) The only general advantage which KMnO₄ and K₂Cr₂O₇ have over cerate is their lower cost.

20E.2. Standardization of Cerate Solutions

There are many ways of standardizing cerate solutions. The following are among the more commonly used methods of standardization.

As₂O₃ is the most reliable primary standard.

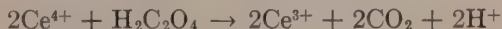


There are 4 eq per mole of As₂O₃. Although the reaction tendency between Ce(IV) and As(III) is very high, the rate of reaction is low, and a catalyst is needed.

Acid solutions of cerate may be standardized with As₂O₃, using OsO₄ (osmium tetroxide) as a catalyst. Only a trace (10⁻⁵ *M*) of catalyst is required, and the reaction proceeds rapidly and smoothly at 25°C, with ferroin as an indicator. The mechanism of catalysis is not definitely known.

Standardization may also be performed in HCl with As₂O₃, using ICl as a catalyst and ferroin as an indicator (see Supplement, p. 851).

Na₂C₂O₄ may be used to standardize cerate solutions.



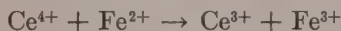
The nature of the acid present affects the rate of this reaction profoundly. In HClO₄ solution, the direct titration of oxalate with cerate is feasible at room temperature, with nitroferroin as an indicator.

In H₂SO₄, the reaction is too slow for direct titration. Instead, a measured excess of cerate is added to the Na₂C₂O₄-H₂SO₄ solution, and the mixture is heated for 5 minutes at 50°C to complete the reaction. The excess cerate is then back-titrated with standard FeSO₄, ferroin

being used as an indicator. In HCl solution, ICl may be used as a catalyst and ferroin as an indicator for the direct titration at 50°C.

Although much qualitative data exists on the rate of the $\text{Ce(IV)}-\text{C}_2\text{O}_4^{2-}$ reaction, there is little quantitative data. The reaction appears to be as complicated as the $\text{Mn(VII)}-\text{C}_2\text{O}_4^{2-}$ reaction, and no mechanism has yet been proposed.

Electrolytic or assayed Fe is occasionally used for standardizing cerate solutions. After dissolution, any Fe(III) is prereduced to Fe(II) , which may be titrated directly at 25°C with cerate.



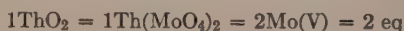
$\text{K}_4\text{Fe(CN)}_6$ serves as a primary standard if powdered and dried to constant weight at 100–110°C. The dried material should be cooled and stored in a desiccator over CaCl_2 (V4). The reaction with cerate requires no catalyst, and proceeds rapidly at 25°C.



20E.3. Determinations with Standard Cerate

Virtually all substances titratable with standard KMnO_4 or $\text{K}_2\text{Cr}_2\text{O}_7$ are also determinable with standard cerate. Table 20.5 gives a list of substances whose determination is described in greater detail in the literature (S18, Y3). The determination of organic compounds is described in the Supplement (p. 852).

Example. Thorium in a 0.600-g sample of an ore is precipitated quantitatively as the molybdate. The precipitate is dissolved in HCl, the Mo is prereduced to Mo(V) , and the solution is then titrated with standard cerate, as outlined in Table 20.5B. Calculate the Th content of the ore as % ThO_2 , if 41.90 ml of 0.1050 *N* cerate are required for titration.



The equivalent weight of ThO_2 is half of the molecular weight.

$$0.1050 \times 41.90 \left| \begin{array}{c} \times \frac{264.04}{2} \\ \text{--- meq cerate = meq ThO}_2 \end{array} \right| \times \frac{100}{600} = 96.8\% \text{ mg ThO}_2$$

20F. OTHER REDOX METHODS

There exist many other kinds of redox methods, none of which are so generally applicable as the permanganimetric, iodimetric, and cerate methods. However, some of these other methods are extremely useful

TABLE 20.5
CERATE TITRATIONS

A. DIRECT TITRATIONS

Substance	Remarks
$\text{H}_3\text{AsO}_3 \rightarrow \text{H}_3\text{AsO}_4$	See page 469.
$\text{H}_3\text{SbO}_3 \rightarrow \text{H}_3\text{SbO}_4$	ICl catalyst at 50°C in HCl. Ferroin. (Without ICl, Sb(III) is potentiometrically titratable in the presence of As(III), provided that the HCl concentration is high.)
$\text{Fe}(\text{CN})_6^{4-} \rightarrow \text{Fe}(\text{CN})_6^{3-}$	See page 470.
$\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}^+ + 2e$	In HNO_3 or HCl solution.
$\text{I}^- \rightarrow \text{ICl}$	In HCl solution. In H_2SO_4 solution, with a potentiometric end point, oxidation product is iodine.
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$	Exp. 20.1 (p. 476).
$\text{Cu}^+ \rightarrow \text{Cu}^{2+}$	Prereducer in Ag reductor.*
$\text{MoO}_3^{2+} \rightarrow \text{MoO}_4^{2-}$	Prereducer to Mo(V) in Ag reductor in 2 M HCl (60–80°C). (Prereducer of Mo compounds in H_2SO_4 with a Zn reductor gives Mo^{3+} .)
$\text{H}_2\text{TeO}_3 \rightarrow \text{H}_2\text{TeO}_4$	Cr(III) catalyst in H_2SO_4 solution. H_2TeO_3 may be titrated in presence of H_2SeO_3 , if H_2SO_4 concentration is not too high.
$\text{Ti}^+ \rightarrow \text{Ti}^{3+}$	HCl concentration must be high for rapid reaction at 25°C.
$\text{Sn(II)} \rightarrow \text{Sn(IV)}$	Prereducer with Ni foil in HCl solution. Use KI-starch indicator, which gives blue color with first slight excess of cerate after all Sn(II) is oxidized. Quite selective.
$\text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-}$	Uncatalyzed oxidation of $\text{S}_2\text{O}_3^{2-}$ by cerate is not stoichiometrical. In presence of KI-starch, $\text{S}_2\text{O}_3^{2-}$ is oxidized stoichiometrically to $\text{S}_4\text{O}_6^{2-}$. KI is both catalyst and indicator.
$\text{Ti}^{3+} \rightarrow \text{TiO}_2^{2+}$	Prereducer in Zn reductor. Diphenylamine indicator.*
$\text{U}^{4+} \rightarrow \text{UO}_2^{2+}$	Prereducer in 4 M HCl in Ag reductor (60–90°C). Only common interferences are Fe, Mo, V, Cu. Prereducer of U compounds in H_2SO_4 with a Zn reductor gives a mixture of U(III) and U(IV), which may be oxidized quantitatively to U(IV) by passing an air stream through the solution before titration.
$\text{VO}_2^{2+} \rightarrow \text{VO}_3^{2+}$	Titrate in H_2SO_4 , HCl, or HClO_4 solution at 50–60°C.
$\text{Hg(I)} \rightarrow \text{Hg(II)}$	50°C.
$\text{N}_2\text{H}_5^+ \rightarrow \text{NH}_4^+ + \frac{1}{2}\text{N}_2 + \text{H}^+ + e$	50°C; Mn(II) catalyst.
$\text{H}_2\text{C}_2\text{O}_4 \rightarrow 2\text{CO}_2 + 2\text{H}^+ + 2e$	See page 469.

B. INDIRECT TITRATIONS

$\text{Al}^{3+}, \text{Mg}^{2+}$	Precipitate with 8-hydroxyquinoline, giving $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$. Dissolve ppt in HClO_4 , reforming 8-hydroxyquinoline, which is determined indirectly.† Empirical; use titer method.
Ca^{2+}	Precipitate CaC_2O_4 , redissolve in HCl or HClO_4 , and determine $\text{H}_2\text{C}_2\text{O}_4$ as in Table A.
K^+	Precipitate $\text{K}_2\text{NaCo}(\text{NO}_2)_6$. Redissolve in H_2SO_4 and determine HNO_2 as below. See Table 20.3B (p. 456) for behavior of Co.
Na^+	Precipitate $\text{NaMg}(\text{UO}_2)_2(\text{C}_2\text{H}_3\text{O}_2)_6 \cdot 6\text{H}_2\text{O}$. Redissolve in H_2SO_4 , and determine UO_2^{2+} as in Table A.
Th^{4+}	Precipitate $\text{Th}(\text{MoO}_4)_2$. Redissolve in HCl and determine Mo as in Table A.
PO_4^{3-}	Precipitate $(\text{NH}_4)_2\text{PO}_4 \cdot 12\text{MoO}_3 \cdot \text{H}_2\text{O}$. Redissolve in HCl and determine Mo as in Table A. Empirical; use titer method.
$\text{HNO}_2 \rightarrow \text{HNO}_3$	†
Zn^{2+}	Add a measured excess of standard $\text{K}_4\text{Fe}(\text{CN})_6$, precipitating $\text{K}_2\text{Zn}_2[\text{Fe}(\text{CN})_6]_2$. Determine excess $\text{K}_4\text{Fe}(\text{CN})_6$ in supernate as in Table A. Not stoichiometric; use titer method.
Cr^{3+}	$6\text{Ce}^{4+} + 2\text{Cr}^{3+} + 7\text{H}_2\text{O} \xrightarrow{\Delta} 6\text{Ce}^{3+} + \text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+$ <p>↑ Excess of standard solution.</p> <p>Determine excess cerate by titration with standard KNO_3, which does not reduce dichromate rapidly enough to interfere with the end point.</p>

*Reduced form easily oxidized by air. Direct titration with standard cerate is best made under inert (CO_2 or nitrogen) atmosphere. Instead, effluent from reductor may be led into excess FeCl_3 , and the Fe(II) formed may be titrated with standard cerate.

†Add a measured excess of standard cerate, and allow time for complete reaction. (Heat is necessary in some cases.) Back-titrate excess cerate with standard FeSO_4 , using ferroin indicator.

for a few kinds of common analyses. Titrations with dichromate and with standard reducing solutions are described in the following sections. Titrations with KBrO_3 are described in the Supplement (p. 853). Titrations have been tried successfully with a great variety of standard solutions, including Mo(III) , Mo(V) , $\text{K}_4\text{Fe(CN)}_6$, ascorbic acid, hydroquinone, V(V) , V(II) , Sn(II) , Hg(I) , Co(III) , Mn(III) , bromine, ICl , IBr , NaClO_2 , NaOCl , Ca(OCl)_2 , NaOBr , $\text{K}_3\text{Fe(CN)}_6$, and Fe(III) , but none appear to possess outstanding advantages over the conventional titrants.

20F.1. Dichromate Titrations

The principal advantages of $\text{K}_2\text{Cr}_2\text{O}_7$ as a standard oxidizing agent are that (1) solutions may be prepared from $\text{K}_2\text{Cr}_2\text{O}_7$ as a primary standard, (2) $\text{K}_2\text{Cr}_2\text{O}_7$ solutions are very stable and may even be boiled for short times without change in titer, (3) $\text{K}_2\text{Cr}_2\text{O}_7$ is only a moderately strong oxidizer which does not oxidize chloride. Hence the chief use of standard $\text{K}_2\text{Cr}_2\text{O}_7$ is in titrating Fe(II) in the presence of chloride. On the other hand, the low oxidizing power of $\text{K}_2\text{Cr}_2\text{O}_7$ is a drawback, for many internal redox indicators are unsuitable with it.

Many reductants may be more advantageously titrated with oxidants other than $\text{K}_2\text{Cr}_2\text{O}_7$, for their uncatalyzed rates of reaction with $\text{K}_2\text{Cr}_2\text{O}_7$ are too low for direct titration. Dichromate has been used for the oxidation of organic compounds in the same way as HClO_4 and Ce(IV) , but the reactions are less stoichiometrical. Many oxidants may be determined by addition of a measured excess of standard Fe(II) , followed by titration of the remaining Fe(II) with standard $\text{K}_2\text{Cr}_2\text{O}_7$. Again, standard $\text{K}_2\text{Cr}_2\text{O}_7$ does not usually have any advantages over other standard oxidants.

More detail is given in the two following sections on the direct titration of Fe(II) and on the indirect determination of Cr .

20F.1a. Direct titration of Fe(II) . The mechanism of the Cr(VI)-Fe(II) reaction is not definitely known, but its present status is summarized by Laitinen (L2). However, the reaction is reasonably rapid, and titration conditions may be selected on the basis of equilibrium considerations alone. The following E 's are known.

$\text{Cl}_2 + 2e \rightleftharpoons 2\text{Cl}^-$	1.36 v
$\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6e \rightleftharpoons 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$ (1 M HCl)	1.09 v
Ferriin (trans. pot., pH 0)	1.06 v
Sodium diphenylamine sulfonate (trans. pot., pH 0)	0.85 v
$\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$ (1 M HCl)	0.70 v
$\text{Fe}^{3+} + e \rightleftharpoons \text{Fe}^{2+}$ (1 M H_2SO_4 and 0.5 M H_3PO_4) ..	0.61 v

It may be seen that dichromate is strong enough to oxidize Fe(II) quantitatively in 1 *M* HCl solution without appreciable oxidation of chloride. Ferroin is unsatisfactory as an indicator, since its transition potential is too close to the formal *E* of the $\text{Cr}_2\text{O}_7^{2-}$ - Cr^{3+} couple in 1 *M* HCl. Sodium diphenylamine sulfonate is a satisfactory indicator, as far as its transition potential is concerned. The use of H_3PO_4 in the titrated solution decreases the *E* of the Fe(II)-Fe(III) couple and thereby increases the sharpness of the end point.

Even in the presence of H_3PO_4 , however, sodium diphenylamine sulfonate does not transit precisely at the equivalence point in the Fe(II)-dichromate titration, and the indicator error is appreciable. This indicator error is most frequently compensated for by use of the titer method, the $\text{K}_2\text{Cr}_2\text{O}_7$ being standardized against primary standard Fe wire (Exp. 20.1).

If used with discrimination, the potentiometric method is probably best for establishing the end point. While the titration of Fe(II) with $\text{K}_2\text{Cr}_2\text{O}_7$ gives a passable inflection in the potentiometric titration curve, the reverse titration of $\text{K}_2\text{Cr}_2\text{O}_7$ with Fe(II) does not. As Fe(II) is added, the *E* of the $\text{K}_2\text{Cr}_2\text{O}_7$ solution slowly increases up to the equivalence point, where a sudden drop in *E* occurs. Just before the equivalence point, several minutes are required for a steady reading after each portion of Fe(II) is added. The platinum indicator electrode does not equilibrate readily with solutions containing an excess of a strong oxidant (see p. 831).

When SnCl_2 is used as a prereductant in the determination of Fe, it is not necessary to remove the excess of SnCl_2 before titrating with standard $\text{K}_2\text{Cr}_2\text{O}_7$, provided that the potentiometric method is used. Sn(II) is a considerably stronger reductant than Fe(II), and the excess Sn(II) may be titrated to a first end point, after which any added $\text{K}_2\text{Cr}_2\text{O}_7$ reacts with Fe(II) until a second end point is reached. The equivalents of $\text{K}_2\text{Cr}_2\text{O}_7$ required to pass between the first and second end points are equal to the equivalents of Fe(II) in the sample. In this titration, the reaction between Sn(II) and any Fe(III) that is formed locally before the Sn(II) equivalence point is slow, and the titration must be performed in hot, highly acid solution. Air must be excluded, because the Sn(II)-Fe(III) reaction induces the air-oxidation of Fe(II). Typical titration curves are shown by Rieman, Neuss, and Naiman (R10).

Hume and Kolthoff (H14) titrate a Sn(II)-Fe(II) mixture with cerate, using cacotheline as a visual indicator for the Sn(II) equivalence point, followed by addition of ferroin and further titration to the Fe(II) equivalence point. Standard $\text{K}_2\text{Cr}_2\text{O}_7$ cannot be used for the Sn(II) equivalence point, because it attacks cacotheline.

Example. A 0.500-g sample of a mineral is treated to extract Fe and to remove interferences. After prereduction to Fe(II), the sample requires 27.13 ml of 0.1000 *N* K₂Cr₂O₇ for titration. Express the Fe content of the mineral as % chalcopyrite (CuFeS₂).

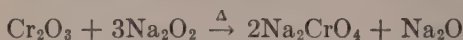
$$1\text{CuFeS}_2 = 1\text{Fe(II)} = 1 \text{ eq}$$

$$0.1000 \times 27.13 \left| \begin{array}{l} \times 183.52 \\ \text{--- mg CuFeS}_2 \end{array} \right| \times \frac{100}{500} = 99.6\% \text{ CuFeS}_2$$

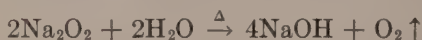
$$\text{--- meq K}_2\text{Cr}_2\text{O}_7 = \text{meq CuFeS}_2$$

20F.1b. Determination of Cr. The principles discussed in the titration of Fe(II) with standard K₂Cr₂O₇ are also applicable to the determination of Cr in ores.

Chromium exists in ores chiefly as Cr₂O₃. One of the principal minerals is chromite, FeO·Cr₂O₃. Chromium is not easily extractable from ores by aqueous or concentrated acid solutions, and a first step in the analysis is to render the Cr leachable by fusion with a flux. An oxidizing flux, such as Na₂O₂, oxidizes the Cr to Na₂CrO₄, which is water soluble.



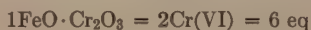
Once cooled, the fused melt is leached with water to extract the Na₂CrO₄, and the excess Na₂O₂ is destroyed by boiling.



The solution is then acidified, an excess of standard FeSO₄ added, and the excess is back-titrated with standard K₂Cr₂O₇. There are 6 eq per mole of Cr₂O₃, as shown in the example below.

In the analysis of a steel for Cr, the sample may be dissolved in dilute H₂SO₄, and Fe and carbonaceous matter oxidized with HNO₃. The Cr is preoxidized to Cr(VI). Commonly used preoxidants are K₂S₂O₈ (Ag⁺ catalyst), HClO₄ (hot, conc.), PbO₂, or KMnO₄. After destruction of excess preoxidant, the Cr(VI) is determined by adding a measured excess of standard FeSO₄ and back-titrating the excess with standard K₂Cr₂O₇.

Example. A 0.500-g ore sample is analyzed for Cr as described above. What is the Cr content as % chromite (FeO·Cr₂O₃), if 5.60 ml of 0.1000 *N* K₂Cr₂O₇ are required for back titration, after addition of 50.00 ml of 0.1052 *N* FeSO₄?



↑ This Fe is oxidized to Fe(III) in preoxidation, and does not interfere in the titration.

$$\begin{aligned}
 \left(\begin{array}{c} \text{meq Fe(II)} \\ \text{reacting with} \\ \text{sought-for Cr(VI)} \end{array} \right) &= \left(\begin{array}{c} \text{total meq} \\ \text{Fe(II)} \\ \text{added} \end{array} \right) - \left(\begin{array}{c} \text{meq standard} \\ \text{K}_2\text{Cr}_2\text{O}_7 \text{ used in} \\ \text{back titration} \end{array} \right) \\
 &= (0.1052 \times 50.00) - (0.1000 \times 5.60) = 4.700 \\
 4.700 &\left| \begin{array}{l} \times \frac{223.84}{6} \\ \times \frac{100}{500} \end{array} \right| = 35.1\% \text{ FeO} \cdot \text{Cr}_2\text{O}_3 \\
 &\quad \left| \begin{array}{l} \text{mg FeO} \cdot \text{Cr}_2\text{O}_3 \\ \text{meq Fe(II) reacting with sought-for Cr(VI) = meq} \\ \text{of FeO} \cdot \text{Cr}_2\text{O}_3 \end{array} \right|
 \end{aligned}$$

20F.2. Standard Reducing Solutions

Not many determinations are based on titrations with reducing solutions, $\text{Na}_2\text{S}_2\text{O}_3$ excepted, since they are generally less stable and less convenient to use than standard oxidizing solutions. In certain analyses, however, the necessity or advantages of using standard reducing solutions may be sufficiently great to warrant the inconveniences. For instance, a sought-for oxidant may be titrated directly with a standard reducing solution, whereas it must be determined indirectly if an oxidizing titrant is used. Fe(II) is a commonly used standard reductant, and is described below. Ti(III) and Cr(II) are useful in certain cases, and are described in the Supplement (p. 855).

The chief advantage of standard FeSO_4 solution is that it does not react rapidly with oxygen in air, and titrations may be made in air without special precautions. Strong oxidants may be determined either (1) by direct titration, or (2) indirectly, by adding an excess of standard FeSO_4 and back-titrating the excess with a standard solution of a suitable oxidant, such as KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, or cerate. Strong reducers that react rapidly with air may be most conveniently determined by the addition of an unmeasured excess of Fe(III). The equivalent amount of Fe(II) formed does not react rapidly with air and may be titrated with a standard oxidizing solution. Titrations with standard FeSO_4 may be followed potentiometrically. Indicators such as ferroin and sodium diphenylamine sulfonate may also be used, the most appropriate indicator depending on the particular oxidant being titrated. Examples of some determinations involving Fe(II) are outlined in Tables 20.3 and 20.5 (pp. 456 and 471).

Because FeSO_4 solutions are slowly oxidized by air, they must be stored out of contact with air. Many arrangements are described in the literature for air-free storage and withdrawal of solutions. Solutions should be restandardized daily. Oxidation by air is catalyzed by solid Fe(OH)_3 , which may be formed by hydrolysis in solutions of low

acidity if there are any traces of Fe(III) present. To prevent precipitation of $\text{Fe}(\text{OH})_3$, standard FeSO_4 solutions are made about 0.2 M in H_2SO_4 .

Since FeSO_4 is not a good primary standard, solutions must be standardized after preparation. Standardization is usually performed by titration against standard $\text{K}_2\text{Cr}_2\text{O}_7$, KMnO_4 , or $\text{Ce}(\text{IV})$. Some workers claim that Mohr's salt, $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, is a good primary standard, but other workers state that its $\text{K}_2\text{Cr}_2\text{O}_7$ titer is about 0.5% less than the theoretical value. Oesper's salt, $\text{FeSO}_4 \cdot (\cdot\text{CH}_2 \cdot \text{NH}_3)_2\text{SO}_4 \cdot 4\text{H}_2\text{O}$, is stated to be superior to Mohr's salt. In using these two salts as primary standards, care is necessary to prevent oxidation both in preparing the salts and in dissolving them.

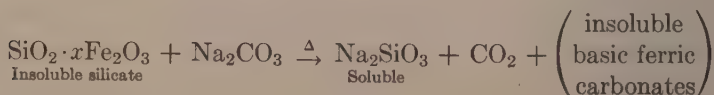
EXPERIMENT 20.1 DETERMINATION OF IRON IN AN ORE

GENERAL OUTLINE

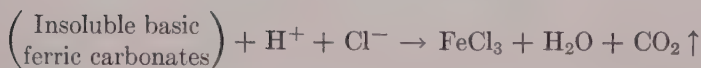
There are three steps in the determination of Fe in an ore: (1) extraction, (2) prereduction, and (3) titration. Each step may be accomplished in several ways.

Extraction. The principal Fe ores are hematite (Fe_2O_3), limonite (hydrated Fe_2O_3), and magnetite (Fe_3O_4). Iron may be efficiently extracted from these ores with hot conc. HCl , but not with conc. H_2SO_4 or HNO_3 . The efficiency of HCl extraction is ascribed to the formation of ferric chloride complexes. Ores also contain Si as SiO_2 and silicates. Iron may be extracted from some kinds of silicates, provided that the sample is finely ground, but the process is slow. SnCl_2 increases the rate of extraction by reducing $\text{Fe}(\text{III})$ to $\text{Fe}(\text{II})$, and is particularly effective for hematites and magnetites.

Some forms of oxides or silicates are not extractable with conc. HCl . If much dark unextracted residue remains after treatment with conc. HCl , the residue is separated from the main extract by filtration, washed, and ignited in a platinum crucible. The residue is then fused with Na_2CO_3 as a flux, which decomposes insoluble silicates.



On acidification with HCl , hydrated SiO_2 precipitates, and the Fe goes into solution. This acidified solution may be combined with the main extract.



The insoluble residue may occasionally be rendered soluble by heating with HF, which volatilizes Si.



The FeF_3 is metathesized to $\text{Fe}_2(\text{SO}_4)_3$ by fuming with conc. H_2SO_4 , and the solution is then added to the main extract.

In some methods of analysis, chloride interferes. In such cases, chloride may be volatilized as HCl by fuming with conc. H_2SO_4 . This is time consuming, and the most popular methods are those which tolerate chloride. A 1:1 HClO_4 - H_3PO_4 solution is superior to HCl, and extracts ores that are poorly extracted by HCl (G2), but it is not recommended for student use (see p. 820).

Prereduction. Proper selection of the prereducing agent does much to avoid interferences. Other elements frequently present in Fe ores are Mn, P (as phosphate), Al, Ca, Mg, Na, K, S, Ti, Cr, and V. Of these, Ti, Cr, and V are reducible to lower oxidation states which may react with the standard solution and cause error.*

Strong reducers like amalgamated Zn should be avoided, since Ti, Cr, and V are reduced to Ti(III), Cr(II), and V(II), which react more readily with standard oxidants than does Fe(II) itself. Another disadvantage of the Zn reductor is that appreciable concentrations of HCl cause gassing (evolution of hydrogen) and must be removed.

SnCl_2 or the Ag reductor does not reduce Ti(IV). Although Cr is reduced to Cr(III), it is not oxidized at an appreciable rate by standard oxidants in acid solution, and causes no error. V is reduced to V(IV), which is oxidized at an appreciable rate by KMnO_4 but not by $\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{Ce}(\text{SO}_4)_2$.

Titration. Titration of the Fe(II) is most frequently performed with $\text{K}_2\text{Cr}_2\text{O}_7$, $\text{Ce}(\text{SO}_4)_2$, or KMnO_4 . The Fe(II)-dichromate titration is discussed on page 472. $\text{Ce}(\text{SO}_4)_2$ possesses all the advantages of $\text{K}_2\text{Cr}_2\text{O}_7$ for the titration of Fe(II), and, in addition, excellent indicators are available, ferroin being used most often. The cerate potentiometric end point is also sharper than the dichromate. The mecha-

*In analysis of samples other than ores, interferences of other reducible elements such as Mo, U, and W must sometimes be considered.

nism of the Fe(II)-permanganate titration is given in the Supplement (p. 841); although it is complicated, study of these details is necessary if the titration is to be performed.

PROCEDURE

From the foregoing discussion, it appears that prereduction by SnCl_2 or the Ag reductor followed by titration with $\text{Ce}(\text{SO}_4)_2$ or $\text{K}_2\text{Cr}_2\text{O}_7$ are the most accurate methods for the determination of Fe, since Ti, Cr, and V do not interfere. In the following determination, SnCl_2 is used as a prereductant, but the student may elect titration with either $\text{Ce}(\text{SO}_4)_2$ or $\text{K}_2\text{Cr}_2\text{O}_7$.

1. *Preparation of standard $\text{K}_2\text{Cr}_2\text{O}_7$.* Dry 2.5–2.6 g of reagent-grade $\text{K}_2\text{Cr}_2\text{O}_7$ in a small weighing bottle for 2 hours in the 150–160°C oven, and store as primary standard material in the desiccator. Weigh out 2.452 g and transfer to the 500-ml volumetric flask. Dissolve in about 400 ml of water, dilute to volume, and mix well. Transfer to a clean, dry 500-ml glass-stoppered bottle for storage. Calculate the normality from the weight of $\text{K}_2\text{Cr}_2\text{O}_7$. (Notes 1, 2.) Standardize the solution with Fe wire (step 3). (Note 5.)

2. *Preparation of standard $\text{Ce}(\text{SO}_4)_2$.* Place 10.4–10.6 g of reagent-grade $\text{Ce}(\text{OH})_4$ in a dry 800-ml beaker, and add 50 ml of conc. H_2SO_4 . Stir well, so that any undissolved solid is uniformly wetted by the acid. Next, slowly add 150 ml of water (CAUTION) over a period of about a minute, stirring well and continuously during the addition and afterwards for about another minute. A clear, red-orange solution of $\text{Ce}(\text{SO}_4)_2$ should result. (Note 3.) Dilute to about 300 ml with water, transfer to a 500-ml volumetric flask, and dilute to the mark. Store in a 500-ml glass-stoppered bottle. (Note 4.) Standardize the solution with Fe wire (step 3). (Note 5.)

3. *Standardization of $\text{K}_2\text{Cr}_2\text{O}_7$ or cerate with Fe wire.* (Note 5.)

3a. Dissolution of the Fe wire. Weigh out three 0.20–0.25-g portions of reagent-grade Fe wire, and transfer each portion to a 500-ml Erlenmeyer flask. (Notes 6, 7.) To each flask, add 10 ml conc. HCl, and cover with a short-stem funnel or watch glass. If there is frothing, wait until it subsides, and then apply heat to increase the rate of solution. When solution is complete, add conc. HCl to bring the volume to 5–10 ml.

3b. Prereduction. (Note 8.) Heat the FeCl_3 solution nearly to boiling and add SnCl_2 (Appendix IV, p. 915) dropwise until the yellow color of FeCl_3 just disappears. Add no more than 1–2 drops in excess. (Note 9.) Dilute to 150 ml, mix well, and then add rapidly 15 ml of 5% HgCl_2 (Appendix IV) while swirling the flask contents. (Notes 10, 11.) Allow the closely covered flask to stand 5 minutes. Then titrate the

Fe(II) immediately, either with $K_2Cr_2O_7$ (step 3c) or cerate (step 3d). (Note 12.)

3c. Titration with $K_2Cr_2O_7$. To the prereduced solution add 15 ml conc. H_3PO_4 . Cool to room temperature under the water tap. Add 2 drops of sodium diphenylamine sulfonate indicator solution. (Appendix IV.) Titrate with $K_2Cr_2O_7$, swirling constantly. (Notes 13, 14.) Calculate the Fe titer of the $K_2Cr_2O_7$ solution. (Note 15.)

3d. Titration with cerate. To the prereduced solution add 10 ml conc. H_3PO_4 and 2 drops of 0.01 *M* ferroin, and titrate with the sulfatocerate solution. (Note 16.) Calculate the Fe titer of the cerate solution. (Note 15.)

4. *Analysis of Fe ore.* Dry the ore sample at 100–105°C for 2 hours. Weigh out three samples into clean, dry, 500-ml Erlenmeyer flasks. (Note 17.) To each sample add 15 ml conc. HCl, and extract as described in Note 18. After extraction is complete, make the volume of solution up to 5–10 ml with conc. HCl, if necessary, and proceed to the prereduction (step 3b), and thence to the titration (step 3c or 3d). Report the average Fe content of the ore as % Fe_2O_3 . (Note 19.)

NOTES

(1) The properties of $K_2Cr_2O_7$ as a primary standard are given on page 440. Show that a 2.452-g sample diluted to 500 ml gives 0.1000 *N* solution.

(2) Later, the dichromate solution is standardized against Fe wire, and the Fe titer thus found is used in the calculations. The primary standard normality is therefore not really required for the Fe ore analysis. However, little additional effort is involved in making up the solution so that its normality is known. If known, the normality provides a fair check on the Fe titer. (Note 15).

(3) If any insoluble material remains, apply heat with the burner, and continue stirring until the residue dissolves.

(4) Reagent $Ce(OH)_4$ (G. F. Smith Chemical Co.) is a mildly dried preparation that dissolves easily. It contains a few per cent of water and cannot be used as a primary standard (D7). The dissolution procedure of step 2 gives a stable solution that is 0.1 *M* in $H_2Ce(SO_4)_3$ and 1.5 *M* in H_2SO_4 . The procedure must be followed closely. If the $Ce(OH)_4$ were dissolved directly in dilute H_2SO_4 , a clear solution would result, but conversion to the sulfatocerate would be incomplete, and basic salts would eventually precipitate.

(5) There are many sources of systematic error in the Fe determination, as brought out in the following notes. An attempt is made to minimize these errors by using the titer method.

(6) Show that each portion requires about 35–45 ml of 0.1000 *N* $K_2Cr_2O_7$ or cerate for titration.

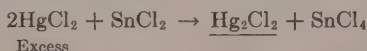
(7) The properties of Fe wire as a primary standard are given on page 440. The wire need not be oven-dried before being weighed. If necessary, remove rust with a fine emery cloth and then wipe free of dust with a clean towel. Before weighing, cut into lengths sufficiently short so that the pieces may lie flat on the bottom of the flask. After dissolution of the Fe wire, there may remain a few small black particles (carbides, silicides) which may be disregarded. If the number of such

particles is large, the wire is of inferior quality. Electrolytic Fe dissolves cleanly.

(8) Work with only one sample at a time, taking it through the titration before starting prereduction of the next.

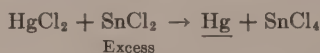
(9) Tip and roll the flask so that the sides are wetted by the SnCl_2 , and so that no FeCl_3 escapes prereduction. This prereduction must be made in fairly concentrated HCl and in hot ($70\text{--}90^\circ\text{C}$) solution, otherwise the rate is low and the reaction may be incomplete. After the excess of SnCl_2 is added, the flask should be kept closely covered with a watch glass, except when adding reagents. If free access of air is permitted, the small excess of SnCl_2 is oxidized quite rapidly, especially in the hot solution, and then the Fe(II) is reoxidized. Reappearance of a yellow color indicates significant reoxidation of Fe(II) , in which case the color should be discharged again with SnCl_2 before going further.

(10) The function of the HgCl_2 is to remove excess SnCl_2 before titration. HgCl_2 is strong enough to oxidize SnCl_2 but not Fe(II) (see TSP). With excess HgCl_2 , a silky white precipitate of Hg_2Cl_2 is formed.



The Hg_2Cl_2 formed is strong enough to reduce Fe(III) during the titration (see TSP), but the rate of this reaction is fortunately too low to cause error. After the end point is reached, the oxidation potential of the titrated solution is high, and the Hg_2Cl_2 may react with the excess oxidant fast enough to cause fading of the end point. Such fading is appreciable with KMnO_4 or cerate as titrants, but not with $\text{K}_2\text{Cr}_2\text{O}_7$.

The HgCl_2 is added rapidly so that it is always in excess. If it is added slowly, or if too much SnCl_2 is present, some metallic Hg may be formed.



Mercury formation is indicated if the Hg_2Cl_2 precipitate is gray, in which case the determination should be rejected. Mercury causes error by reducing Fe(III) at an appreciable rate during the titration, and also causes faster fading of the end point than does Hg_2Cl_2 .

If no precipitate forms on the addition of HgCl_2 , reduction of Fe(III) is probably incomplete. Such a determination should also be rejected.

(11) Tip and roll the flask so that the sides are wetted by the HgCl_2 solution, and so that no SnCl_2 remains unoxidized. Continue to keep the flask covered with the watch glass.

(12) Air-oxidation of Fe(II) is not rapid at room temperature, but may be appreciable if the titration is delayed.

(13) The indicator blank is small but appreciable, amounting to less than a few hundredths of a milliliter of $0.1\text{ N K}_2\text{Cr}_2\text{O}_7$. The blank cannot be easily determined, for the indicator action requires the presence of Fe(II) (K18). The indicator correction is not determined, because the titer method is used.

(14) The Cr(III) formed during titration gives the solution a greenish color before the end point. In such a solution, the indicator changes to a gray-green just before the end point. The end point is the first perceptible tinge of violet which persists after the solution is swirled for 10 seconds.

(15) For excellent work, the relative range of triplicate determinations should be less than 0.3%. It is instructive to calculate the normality from the Fe titer, and to compare it with the primary standard value. The Fe titer value may be several tenths of a per cent higher.

(16) When added to the faintly green or colorless Fe(II) solution, the ferroin imparts a brown-orange color. At the end point, the color changes sharply from brown-orange almost to colorless. The oxidized form of the indicator is a very faint blue. FeCl₃ is yellow, and would ordinarily hinder perception of the end point, but the H₃PO₄ converts Fe(III) to colorless phosphate complexes.

If Hg₂Cl₂ is present from the SnCl₂ prereduction, it slowly oxidizes the excess Ce(IV) after the end point has been reached, and the brown-orange color slowly returns. The end point is reached when the brown-orange color does not return for 10 seconds while the flask is swirled.

(17) The sample size should be such as to require 35–45 ml of 0.1 N K₂Cr₂O₇ or cerate for titration. Show that the proper sample size for an ore containing 50–60% Fe₂O₃ is 0.56–0.60 g. Sample preparation is described in the Supplement (p. 858).

(18) The following details should be observed to promote speedy and complete extraction. (a) The sample should be completely wet and in uniform suspension before heat is applied to the flask. If the sample remains caked on the sides of the vessel, baking into large aggregates may occur. The Fe cannot be easily extracted from these aggregates. (b) Complete extraction is indicated when only grayish, flocculent silica particles remain. These are easily distinguished from the dark, dense particles of the original ore. A small number of unattacked particles may be ignored. If an appreciable unattacked residue remains, treatment with HF or Na₂CO₃ is necessary. Such treatment is not required for student samples unless specified by the instructor. (c) If SnCl₂ is used as a prereductant, it may also be used to speed the extraction process. During extraction SnCl₂ solution is added dropwise barely to keep the yellow FeCl₃ color discharged. With SnCl₂, leaching of hematites and magnetites may be practically completed in 5–10 minutes if the system is swirled continuously over a burner. When extraction is complete, the yellow FeCl₃ color is restored, if necessary, by heating with access to air. The solution is then prereduced and titrated, starting with step 3b.

Alternatively, the sample may be heated for only a few minutes as described above, and the closely covered flask left overnight on the hot plate. The solution must not be allowed to go to dryness.

(19) For excellent work, the relative range of triplicate determinations should be less than 0.3%, and the relative error of the average should be less than 0.3% for most ores. When real ore samples are extracted by the simple techniques of this experiment, errors at the 0.1% level cannot generally be expected.

EXPERIMENT 20.2. DETERMINATION OF CALCIUM IN LIMESTONE

GENERAL DISCUSSION

Limestones have the following composition:

CaO.....	30–45%	Mn	}	{ Usually less than 0.2% each
MgO.....	10–25%	Ti		
Na ₂ O.....	0–3%	P		
K ₂ O.....	0–3%	CO ₂		30–45%
Al ₂ O ₃	0–5%	SiO ₂		1–20%
Fe ₂ O ₃	0–2%			

There exist several systematic schemes for the complete analysis of a limestone for each of its major constituents (H8). Such schemes are best studied in the intermediate analytical course, along with the gen-

eral topics of separations and analysis of mixtures. However, there also exist short procedures for the determination of single constituents, and these may profitably be studied in the elementary course. The following determination of Ca is an example of such a short procedure.

OUTLINE OF THE METHOD

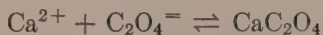
1. The sample is extracted with hot HCl, which not only dissolves CaCO_3 but also breaks down some silicates. The breaking down of silicates is aided by a prior ignition of the sample. After this treatment most of the metallic constituents of the sample are in solution, but Si exists mostly as insoluble SiO_2 .



2. The solution is diluted and $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is added. This causes no precipitation of CaC_2O_4 , because oxalate is bound as $\text{H}_2\text{C}_2\text{O}_4$ in the acid solution and the solubility product of CaC_2O_4 is not exceeded.

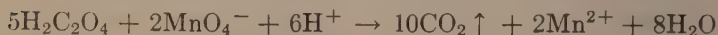
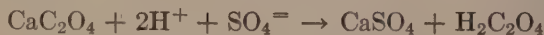


3. The solution is slowly neutralized with NH_3 to pH 3.7–4.3, whereupon CaC_2O_4 precipitates quantitatively. Fe(III) and Al(III) form very stable oxalate complexes and remain in solution. $\text{Mg}_2\text{C}_2\text{O}_4$, although insoluble, remains in the supersaturated condition and does not precipitate, provided that the digestion time is kept short.



4. The CaC_2O_4 precipitate (together with SiO_2) is filtered through a Gooch crucible and washed sparingly, since CaC_2O_4 is only moderately insoluble.

5. The washed CaC_2O_4 is metathesized with dilute H_2SO_4 , and the $\text{H}_2\text{C}_2\text{O}_4$ liberated is then titrated with standard KMnO_4 . Inspection of the equations shows that the equivalent weight of Ca is one-half the formula weight.



ERRORS AND INTERFERENCES

The relative standard deviation of a single determination is about 0.1%, for both dolomitic and argillaceous limestones (L11).

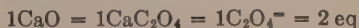
The requirement of this method is that there be 1 mole of oxalate carried along per mole of Ca in the original sample, right up to the titration step. Even gross amounts of inert impurities, such as SiO_2 , cause no error if they contain neither Ca nor oxalate. (This is not the case when the CaC_2O_4 is weighed.)

Since the solution contains excess oxalate, the most likely source of error is coprecipitation of oxalates other than CaC_2O_4 , which will give high results. Conditions are designed to minimize such coprecipitation. Since there is a large excess of NH_4^+ , and since the solution is quite acid, the coprecipitated oxalates are probably predominantly $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and $\text{H}_2\text{C}_2\text{O}_4$, both of which are soluble and are removed in washing. Mn(II) and TiO(II) are the only constituents which show any tendency to be appreciably coprecipitated, and both of these have been proved tolerable in proportions far greater than those which exist in limestones. (Amounts of Mn and Ti up to 2% of the amount of Ca cause less than 0.1% error.) Postprecipitation of MgC_2O_4 is probably the greatest potential source of error, but with careful work, reprecipitation is unnecessary.

Since oxalate is in excess, and since the solution is quite acid, coprecipitation of Ca compounds other than CaC_2O_4 (which will give low results) is not very likely. Thus even amounts of phosphate comparable to the amount of Ca cause no significant error. The procedure of adding NH_3 slowly to an acid solution containing Ca and oxalate causes precipitation of CaC_2O_4 from a solution in which the solubility of CaC_2O_4 is high; this gives a well-formed crystalline precipitate and a minimum of coprecipitation. Were the precipitation made by adding $(\text{NH}_4)_2\text{C}_2\text{O}_4$ to a neutral CaCl_2 solution, contamination would be high. Holth (H10) has made a careful study of the optimum conditions for precipitating CaC_2O_4 , and of the effect of interfering substances.

Recently, Watts has recommended precipitation in ammoniacal medium, with sodium gluconate, a complexing agent that prevents coprecipitation of other metal oxalates. Errors appear to be definitely lower than for the precipitation at low pH (W6).

Example. By the foregoing method of analysis, a 0.2500-g sample of a limestone requires 44.68 ml of 0.1000 N KMnO_4 for titration. What is the Ca content as % CaO?



Hence the equivalent weight of CaO is 56.08/2, or 28.04.

$$\begin{array}{c}
 0.1000 \times 44.68 \left| \begin{array}{l} \times 28.04 \\ \times \frac{100}{250.0} \end{array} \right| = 50.1\% \text{ CaO} \\
 \left| \begin{array}{l} \text{mg CaO} \\ \text{meq KMnO}_4 = \text{meq CaO} \end{array} \right| \quad \text{\% CaO}
 \end{array}$$

PROCEDURE

1. *Preparation of standard KMnO_4 .* Dissolve about 3.0 g of reagent-grade KMnO_4 in about 950 ml of distilled water in a beaker or flask. Cover closely with a watch glass, and heat the contents almost to boiling for an hour. Set in the locker to age overnight. Filter through a coarse sintered glass crucible. (Notes 1, 2.) Store the solution in a clean glass-stoppered bottle, and keep in the darkened locker except when withdrawing solution. Clean all glassware soon after use. (Note 3.)

2. *Standardization of KMnO_4 .*

2a. Dry about 1.5 g of reagent-grade $\text{Na}_2\text{C}_2\text{O}_4$ at 105–110°C for an hour. Weigh accurately a 1.2–1.5-g portion of the dried $\text{Na}_2\text{C}_2\text{O}_4$ into a 250-ml volumetric flask, dissolve, dilute to volume, and mix well. (Notes 4, 5.)

2b. Transfer a 50-ml aliquot of the standard $\text{Na}_2\text{C}_2\text{O}_4$ solution to a 250-ml beaker, add 50 ml of water containing 5–6 ml of conc. H_2SO_4 , and titrate by the procedure of step 2c or 2d. (Note 6.)

2c. Approximate titration by the McBride procedure. Using a thermometer as a stirring rod, heat the solution to 90°C. (Notes 7, 10.) Titrate the hot solution with the KMnO_4 , taking as the end point the first perceptible tinge of pink which persists for at least a half-minute. (Note 8.)

2d. Titration by the Fowler and Bright procedure. From the results of the approximate titration estimate the volume of KMnO_4 required for another 50-ml aliquot of $\text{Na}_2\text{C}_2\text{O}_4$. Begin the titration by adding about 95% of the required amount of KMnO_4 . (Note 9.) Before titrating further allow the beaker to stand until the color of the KMnO_4 disappears. Then heat to 55–60°C and complete the titration. (Notes 10, 11.) Determine the blank on a system (at 55–60°C) containing 100 ml of water and 5–6 ml of conc. H_2SO_4 . Titrate 3 aliquots of the $\text{Na}_2\text{C}_2\text{O}_4$ solution by the Fowler and Bright procedure, and calculate the KMnO_4 normality. (Note 12.)

3. *Preparation of the sample.*

3a. Dry the sample at 100–110°C for 2 hours. (Note 13.)

3b. Into three clean, dry, unweighed crucibles, weigh by subtraction triplicate 0.28-g samples of the dried limestone. (Notes 14, 15.)

3c. Cover the crucibles and ignite. (Notes 16, 17.)

3d. After ignition, set the crucible with the sample upright inside a 250-ml beaker. Keeping the beaker covered as closely as possible with a watch glass, add 5 ml of water to the crucible contents, and then slowly add 10 ml of conc. HCl with a dropper. After addition of the HCl is complete, tip the crucible over within the beaker, and heat just to boiling for 5–10 minutes to complete the extraction of Ca. The

crucible should be rolled around gently in the beaker, so that all parts of it are wetted by the hot solution.

3c. Add 5 drops of saturated bromine water. Then withdraw the crucible, rinse, and boil the beaker contents gently for 5 minutes to expel excess bromine. (Notes 18, 19.)

4. *Precipitation and isolation of the CaC_2O_4 .* (Note 20.)

4a. Saturate 100 ml of water with 5 g of solid $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, and filter through fine paper. Heat this solution to about 90°C and add it to the sample solution, which should also have been heated to about 90°C .

4b. To the still hot (approximately 80°C) solution, add 3 drops of methyl orange indicator. Add 6 *M* NH_3 at a rate of 1 drop per few seconds, with constant stirring, until a *pH* of 3.7–4.3 is attained. (Note 21.) Digest 20–30 minutes. (Note 22.)

4c. Decant the mother liquor through an unweighed Gooch crucible having an asbestos mat. (Note 23.) When the mother liquor is decanted, add 20 ml of cold 0.02 *M* $(\text{NH}_4)_2\text{C}_2\text{O}_4$ –0.01 *M* $\text{H}_2\text{C}_2\text{O}_4$ to the beaker. Roll this wash portion around the inside of the beaker, stirring the remaining precipitate with a glass rod, and then decant the wash portion through the filter crucible. Repeat the washings with two more 20-ml portions of 0.02 *M* $(\text{NH}_4)_2\text{C}_2\text{O}_4$ –0.01 *M* $\text{H}_2\text{C}_2\text{O}_4$. Next wash the precipitate in the beaker and in the Gooch crucible with four successive 7-ml portions of cold water in similar manner (Note 24), taking care that each portion wets the sides of the beaker and filter crucible.

4d. Remove the filter crucible from the filter funnel, and rinse the outside with a stream from the wash bottle. Place the whole crucible into the 250-ml beaker containing the untransferred portion of the precipitate.

5. *Titration of the CaC_2O_4 .*

5a. Add 50 ml of water to the beaker containing the crucible, asbestos mat, and CaC_2O_4 . With a thermometer as a stirring rod, disperse the asbestos and precipitate throughout the solution. Do not remove the crucible from the system. Then, while stirring, add 50 ml of water containing 5–6 ml of conc. H_2SO_4 .

5b. Titrate the first of the three samples with standard KMnO_4 by the McBride procedure, as in step 2c.

5c. Using the result of the titration of step 5b, estimate the quantities of standard KMnO_4 that will be required for each of the two remaining samples. Titrate these by the Fowler and Bright procedure of step 2d. (Note 25.)

5d. Calculate the average Ca content as % CaO from the duplicate titrations by the Fowler and Bright procedure. (Note 26.)

NOTES

(1) Distilled water contains organic material which is slowly oxidized by KMnO_4 , changing the titer of the solution. The solution is heated and aged to remove this oxidizable material before standardization. In the oxidation MnO_2 is produced, and must be removed before standardization. Heating and aging coagulate the MnO_2 , so that only a coarse filter is necessary. A Gooch crucible may be used if sintered glass is not available, but the first 50 ml of filtrate should be rejected, since the asbestos may contain traces of oxidizable material. Paper filters cannot be used. A safety flask must be used between the filter flask and aspirator, since much organic matter may be carried from the rubber tubing if water backs into the flask.

(2) Solutions aged for 2-3 weeks before filtration are more stable than those aged only overnight. The latter are acceptable for student work, provided that they are standardized and used within a few days after preparation. After this, precipitation of MnO_2 occurs and the titer changes appreciably.

(3) KMnO_4 solutions often leave films of MnO_2 on vessels. Freshly precipitated MnO_2 may be easily removed by rinsing the vessel first with tap water and then with a warm $\text{Na}_2\text{C}_2\text{O}_4\text{-H}_2\text{SO}_4$ solution. The solution is prepared by adding 10 ml of conc. H_2SO_4 slowly to 40 ml of water, and then dissolving 1-2 g of $\text{Na}_2\text{C}_2\text{O}_4$ therein. This solution may be used for many rinsings, and should be kept on hand for cleaning apparatus while KMnO_4 titrations are made. Dried MnO_2 is much harder to remove, and scouring is usually necessary.

(4) Show that a 50-ml aliquot of this solution requires about 35-45 ml of 0.1 N KMnO_4 for titration.

(5) $\text{Na}_2\text{C}_2\text{O}_4$ solution is not very stable in storage, and should be used within a few days after its preparation.

(6) It is recommended that only the first of a series of samples be titrated by the McBride procedure, which may give more erratic results than the Fowler and Bright procedure. When the approximate volume of KMnO_4 required for titrating the sample is learned from the first titration, the Fowler and Bright procedure is easy to perform.

(7) The temperature should not fall outside the range 60-90°C for this titration. Care should be exerted not to hit the thin-walled thermometer bulb against the sides of the beaker while stirring.

(8) Add only 2-3 drops of KMnO_4 at the beginning of the titration, and wait until the solution is decolorized before proceeding. The KMnO_4 should be added slowly during titration, with good swirling and occasional interruption to allow decolorization of the solution. If it is added too rapidly, error-causing side reactions are likely to occur.

(9) Add the initial portion of the KMnO_4 solution at room temperature, with the buret wide open, letting the stream fall directly into the oxalate solution, which should not be stirred. To prevent splashing, the buret tip should be only a half-inch above the surface of the solution.

(10) Be careful not to superheat the sides of the beaker above the solution, for this promotes the decomposition of $\text{Na}_2\text{C}_2\text{O}_4$.

(11) In finishing the titration, add the KMnO_4 drop by drop, stirring gently, and waiting after each drop until the solution is decolorized before adding the next drop. If KMnO_4 is added too rapidly, error-causing side reactions are likely to occur.

(12) The range of triplicate titrations should be less than 0.05 ml for excellent work.

(13) Higher drying temperatures are not recommended. MgCO_3 is often a major component of limestone, and decomposes rapidly at 230°C.

(14) For samples containing 30–45% CaO, show that the recommended sample size requires 30–45 ml of 0.1 *N* KMnO_4 for titration. If samples of different composition are used, the instructor will announce the proper sample size. (See Supplement, p. 858, for sample preparation.)

(15) If marked or stained crucibles must be used, they should first be boiled for 15 minutes in conc. HCl, in order to extract metallic impurities that might otherwise interfere.

(16) The crucibles should be slowly brought to the maximum temperature with the Bunsen burner, about 5 minutes being taken to achieve this temperature. Slow heating of the sample is necessary to prevent boiling and spattering due to rapid decomposition of MgCO_3 . The sample may then be ignited for a half hour at the full heat of the Meker burner, or in the electric furnace at 900–950°C. Examine the crucible covers after ignition for evidence of spattering. Platinum crucibles are best for this ignition, but porcelain crucibles are adequate.

(17) The purpose of ignition is to decompose silicates, rendering the Ca more extractable. This is an adequate measure only for certain types of limestones containing small amounts of SiO_2 . For some types of siliceous limestones, fusion with Na_2CO_3 is necessary to break down silicates. Fusion with Na_2CO_3 must be performed in Pt crucibles. On the other hand, some kinds of limestones do not require ignition. The sample may be weighed directly into the beaker and decomposed by adding HCl. The ignition may be omitted if the instructor so directs.

(18) Bromine oxidizes any Fe(II) to Fe(III). Fe(II) would interfere by precipitating as FeC_2O_4 with the sought-for CaC_2O_4 . Fe(III) remains in solution, being complexed by the excess oxalate.

(19) Withdraw the crucible as follows: With a glass rod, hold the crucible gently against the side of the beaker, so that the crucible is out of the solution. Wash the acid solution from the upper edge of the crucible with the wash bottle, and then grasp the crucible by the washed part with the tongs. Rinse the crucible and rod well with the wash bottle, letting the rinsings fall into the beaker. The tongs should be held uppermost so that the wash stream does not run over them.

(20) This step should not be begun unless the titrations may be performed on the same day.

(21) This pH corresponds to an intermediate orange color of methyl orange. The color tint is best determined by comparison with 150 ml of a pH 4 buffer solution, also containing 3 drops of methyl orange indicator. Such a solution should be labeled and set out on the reagent shelf by the instructor.

(22) This is sufficient for complete precipitation of CaC_2O_4 , but not long enough for appreciable postprecipitation of MgC_2O_4 .

(23) Since the washed Gooch crucible and precipitate are eventually retransferred to the 250-ml beaker for titration, complete transfer of the precipitate from the beaker to the crucible is unnecessary. The only purpose of this filtration is to separate the mother liquor with its excess oxalate from the precipitate; it is not intended that the precipitate be quantitatively transferred to the filtering crucible. Even if available, a sintered crucible should not be used, because of difficulty that is encountered later in removal of the precipitate.

(24) The washing must be restricted because of the appreciable solubility of CaC_2O_4 . It is desirable, but not necessary, to cool the wash water in an ice bath before use.

(25) Determine the blank by finding the volume of standard KMnO_4 required to titrate at 55–60°C a system containing 100 ml of water, 5–6 ml conc. H_2SO_4 , and an amount of asbestos equal to that used to prepare the filter crucible.

(26) For excellent work, the relative range of duplicate determinations should be less than 0.3%, and the relative error of the average should be less than 0.3% for most limestones. The principal sources of error lie in incomplete extraction and in losses of the CaC_2O_4 precipitate.

EXPERIMENT 20.3. DETERMINATION OF COPPER IN AN ORE

GENERAL OUTLINE

Extraction. Copper exists in its most important ores as sulfides, oxides, and basic carbonates. While some of these minerals yield to other acids, sulfides must be decomposed with HNO_3 . Extraction with HNO_3 is rapid because sulfide is oxidized to free sulfur.

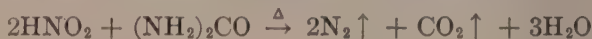


However, ores containing much Fe are not effectively decomposed by HNO_3 and must be treated with HCl.

After extraction, all N oxides and HNO_2 must be removed, or they later catalyze the air-oxidation of iodide in the titration, giving high results for Cu. Even HNO_3 must be reduced to a fairly low concentration; high nitrate concentrations in the titration step may oxidize iodide slowly, giving traces of N oxides.

The classical procedure for removing HNO_3 , N oxides, and HNO_2 is to fume with conc. H_2SO_4 . The use of H_2SO_4 in conjunction with HCl and HNO_3 has added advantages: it oxidizes and volatilizes any sulfur formed in the ore decomposition, and its high boiling temperature improves the extraction.

On the other hand, there are many samples that dissolve easily in dilute HNO_3 , or in aqua regia, and for which the solvent action of fuming with H_2SO_4 is unnecessary. For such samples, HNO_2 and N oxides* may be most easily removed by boiling with urea.



HClO_4 is a most efficient extractant for Cu, and saves considerable time and effort. Neither free sulfur nor N oxides are formed. Sb and As are oxidized by HClO_4 to the noninterfering pentavalent states.

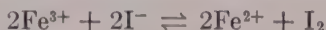
Interferences. The principal accompanying elements in most Cu ores are Fe, As, Sb, Al, and Si. Ag, Pb, Bi, Cd, and Zn are occasionally present. Al, Si, Bi, Cd, and Zn do not interfere. Ag and Pb are largely

*N oxides are in equilibrium with HNO_2 in aqueous solutions in contact with air.



removed by precipitation if HCl is used in the extraction step; if not so removed, they precipitate as insoluble noninterfering iodides in the titration step. (If present in much larger amounts than usually found in ores, the yellow AgI and PbI₂ precipitates may obscure the end point.)

Fe(III) interferes by oxidizing iodide, and gives high results for Cu.



It is troublesome to remove Fe as Fe(OH)₃, since Cu is coprecipitated. Instead, in the Park method, Fe(III) is tightly complexed with fluoride, forming FeF₆³⁻ and decreasing the oxidizing strength of Fe(III) sufficiently to prevent oxidation of iodide (P1).

Sb(III) and As(III) would interfere by reducing iodine in the titration step.



However, under the oxidizing conditions of the extraction, only As(V) and Sb(V) are formed. The latter might also interfere in the titration step by oxidizing iodide, according to the reverse of the preceding reaction. Such interference is prevented by carrying out the titration at low acidity (pH above 3.5).

A study of other interferences is given by Meites (M13) and Park (P1). When there are large amounts or many kinds of interferences, it may be more opportune to remove the sought-for Cu from the bulk of interferences. One way is to precipitate the Cu as metal on a strip of Al, leaving most of the interferences (Fe, As, Sb, V, U, Mo) behind in solution.



For titration, the Al strip with the adhering Cu is dissolved in HNO₃.

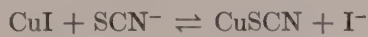
Iodimetric titration. An excess of KI is added, liberating iodine, which is titrated with standard Na₂S₂O₃, starch being used as an indicator.



Cu(II) is not normally a strong enough oxidant to oxidize I⁻, but the oxidation occurs because of the insolubility of the product, CuI.* (See TSP.) If the pH is above 4.5, Cu(II) may be appreciably hydrolyzed or even precipitated as Cu(OH)₂, decreasing its oxidizing strength sufficiently to prevent complete oxidation of I⁻, and giving a diffuse end point. This fact, together with the interference of As and Sb, demands that the titration be performed at pH 3.5–4.5.

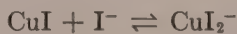
*Cuprous salts are normally not stable in air, but the insolubility of CuI prevents its oxidation.

Iodine has a great tendency to be adsorbed irreversibly on CuI, coloring it and causing a lagging end point. To prevent such error, KSCN is added just before the end point, metathesizing the CuI to less soluble CuSCN, and liberating the adsorbed iodine. The titration may then be completed to a sharper and more accurate end point.



KSCN must be withheld until just before the end point; if it is added while there is still appreciable iodine, or if much time passes before the end point is reached, iodine oxidizes thiocyanate, giving low results for Cu.

Meites (M13) describes another way of performing the titration to eliminate all error due to coprecipitation on CuI or to instability of thiocyanate. If a large amount of KI is added, the CuI first formed redissolves to form CuI_2^- , giving a clear colorless solution and a very sharp end point.



Extensions of the iodimetric determination of Cu. This method may also be used to determine Cu in brass, which does not contain appreciable amounts of interfering Fe, As, and Sb. Tin, a major constituent of brass, precipitates as SnO_2 when the sample is dissolved in HNO_3 . If the SnO_2 is separated for determination, special measures must be taken to recover coprecipitated Cu. If the determination of SnO_2 is not necessary, it may be left in the system, for it does not interfere in the iodimetric determination of Cu; the coprecipitated Cu appears to be liberated before titration, and the error is negligible (M13).

Example. What is the Cu content, as % CuO, of 2.000 g of an ore which requires 42.65 ml of 0.1000 N $\text{Na}_2\text{S}_2\text{O}_3$ for titration by the iodimetric method?

From the chemical equations we obtain

$$1\text{CuO} = 1\text{Cu}^{2+} = \frac{1}{2}\text{I}_2 = 1\text{S}_2\text{O}_3^{2-} = 1 \text{ eq}$$

$$0.1000 \times 42.65 \left| \begin{array}{l} \times 79.54 \\ \times \frac{100}{2000} \end{array} \right| = 16.96\% \text{ CuO}$$

$\left| \begin{array}{l} \text{mg CuO} \\ \text{meq Na}_2\text{S}_2\text{O}_3 = \text{meq CuO} \end{array} \right|$

PROCEDURE

1. *Preparation of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$.* Boil 525 ml of water in a 1-l Florence flask for about 5 minutes. Cool under tap water and add 0.25 g Na_2CO_3 and 12–13 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$. (Note 1.) Allow the solution to age at least 1 day before standardization. (Note 2.)

2. *Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ with Cu.* (Note 3.)

2a. Weigh out accurately four 0.22–0.29-g portions of Cu wire or foil, and place each portion in a 250-ml Erlenmeyer flask so that the pieces lie flat on the bottom. (Notes 4, 5.) To each flask add 10 ml water and 5 ml conc. HNO_3 . Warm gently until the Cu dissolves. Then boil gently for 5 minutes to remove N oxides.

2b. Add water to give 30–50 ml of solution. Then add 5 ml of 4% urea solution and boil for a minute to remove N oxides. (Note 6.)

2c. Neutralize the solution by the drop-by-drop addition of conc. NH_3 . (Note 7.) Then add 3.0 g NH_4HF_2 , swirl the flask contents until any remaining precipitate is a pale greenish-white, and go without delay to step 2d. (Notes 8, 9.)

2d. Add 3.0 g KI, swirl gently, and begin titration with $\text{Na}_2\text{S}_2\text{O}_3$. Titrate until the brown iodine color begins to fade, and until the CuI precipitate is a light-buff color. Then add 3 g KSCN, swirl the flask until the crystals are dissolved, add 5 ml of starch indicator, and complete the titration. (Notes 10–12.)

2e. Calculate the average Cu titer of the $\text{Na}_2\text{S}_2\text{O}_3$ solution. (Note 13.)

3. *Analysis of the ore sample.* (Note 14.)

3a. Dry the sample for 2 hours at 100–110°C. Into 250-ml flasks weigh triplicate 1.3–1.4-g portions of the sample to the nearest milligram. (Note 15.)

3b. To each flask add 5 ml conc. HCl and 10 ml conc. H_2SO_4 , swirl the sample into uniform suspension, and then evaporate over the Bunsen flame until dense white fumes of H_2SO_4 appear. (Note 16.)

3c. Cool the flask under the water tap and then add 1 ml conc. HNO_3 (CAUTION), and 5 ml conc. HCl (CAUTION). Heat cautiously to prevent loss by effervescence, and evaporate to dense white fumes. (Note 17.)

3d. Cool, add 30 ml of water and 10 ml of saturated bromine water, and boil gently for 3 minutes to expel all bromine. (Notes 18, 19.)

3e. Proceed to steps 2c and 2d. (Note 20.) Report the average % Cu in the sample. (Note 21.)

NOTES

(1) The water is boiled to remove oxygen and CO_2 and to destroy bacteria, all of which cause decomposition of $\text{Na}_2\text{S}_2\text{O}_3$. Na_2CO_3 is a preservative that reduces the rate of growth of bacteria during storage.

(2) Time is allowed for residual impurities to react with the $\text{Na}_2\text{S}_2\text{O}_3$, so that a steady concentration is reached. Even carefully prepared $\text{Na}_2\text{S}_2\text{O}_3$ solutions change on standing, and should be restandardized every few days. Work should therefore be planned to perform both standardization and sample titration within a few days, or preferably on the same day.

(3) Since the titer method is used, the procedure for standardization is the same as for ore samples. Optionally, to make the standardization more closely resemble the titration of the ore sample, 2 ml of 0.33 *M* ferric nitrate may be added during dissolution of the Cu metal.

(4) This weight of foil requires about 35–45 ml of 0.1 *N* $\text{Na}_2\text{S}_2\text{O}_3$ for titration.

(5) The Cu need not be oven-dried. Remove tarnish with a fine emery cloth if necessary, and wipe off dust and abrasive with a clean cloth.

(6) Urea is used to remove HNO_2 and N oxides. Enough urea solution for all determinations may be prepared by dissolving 1 g in 25 ml of water.

(7) Too much NH_3 at this point leads to too high a pH in the buffered solution later, and to a fading end point. For the pure Cu solution containing no Fe, add NH_3 dropwise until the deep blue of the $\text{Cu}^{2+}\text{-NH}_3$ complex just forms and remains when the solution is swirled constantly. Then barely discharge any deep-blue color to greenish, if necessary, with a drop of conc. H_2SO_4 . Basic Cu salts may or may not precipitate when NH_3 is added, but they cause no difficulty.

Martin (M9) gives a procedure in which methyl orange is used to perform the neutralization.

With ore samples, brown $\text{Fe}(\text{OH})_3$ obscures the color changes, and the following technique must be used in neutralization. As NH_3 is first added, pure reddish brown $\text{Fe}(\text{OH})_3$ is formed. As more NH_3 is added, the flask contents begin to acquire a blackish hue, indicating that the deep-blue complex has begun to form. Boil the solution gently for a half-minute in order to give a coagulated precipitate that settles readily. Let the flask stand for a minute or two, or until the color of a thin layer of the supernate can be seen. Then discharge any deep-blue color to greenish, if necessary, by the dropwise addition of conc. H_2SO_4 , shaking the flask and letting it stand after each drop, so that the color of the supernate may be observed.

(8) One function of NH_4HF_2 is to prevent interference by Fe(III). About 1 g NH_4HF_2 is required per 0.1 g of Fe or Al in the sample. For samples containing large amounts of Fe or Al, more NH_4HF_2 should be used. The other function of NH_4HF_2 is to buffer the solution at pH 3.3–4.0. KHP is sometimes used as a buffer in addition to NH_4HF_2 , but this is unnecessary (C11).

After NH_4HF_2 is added, some undissolved basic Cu salts may remain. These cause no difficulty, since they dissolve rapidly when KI is added.

(9) Before addition of NH_4HF_2 , the determination may be interrupted at any time. After NH_4HF_2 is added, complete the titration before adding NH_4HF_2 to the next sample.

(10) After KSCN and starch are added, the suspension becomes blue-gray before the end point. The end point is the sharp change from blue-gray to an off-white, and should be permanent for at least a minute. A fading end point (i.e., a slow return of the blue color) may be caused by too much NH_3 or too little NH_4HF_2 in step 2c.

(11) When the titration is finished, rinse the flask immediately to prevent its being etched by the acid fluoride solution.

(12) The blank may be appreciable, and may be contributed to not only by the indicator but also by iodate in the KI and by reducing impurities in the KSCN. Proper determination of the blank is troublesome. The titer method partially compensates for the blank.

(13) The first of the four determinations may be rejected as a practice run, and the relative range of the remaining triplicates should be less than 0.2% for excellent work.

(14) The extractant in this procedure is $\text{HCl-HNO}_3\text{-H}_2\text{SO}_4$. If the student samples are more easily extractable, the instructor will furnish special directions.

(15) If the Cu content ranges from 17 to 20%, this sample size requires about 35–45 ml of 0.1 N $\text{Na}_2\text{S}_2\text{O}_3$ for titration. For samples of different composition, the instructor will announce the proper sample size. Sample preparation is described in the Supplement (p. 858).

(16) HCl is added before HNO_3 in order to minimize the size of the sulfur bead by volatilizing as much sulfide as possible. To avoid loss by bumping, swirl the flask contents constantly during evaporation, which need take no more than a few minutes. Hold the flask in a clamp with no rubber on the jaws, and apply the flame directly not only to the bottom of the flask, but also to the sides, to prevent condensation and to speed evaporation. All fuming must be done in a good hood.

(17) The HCl-HNO_3 mixture is aqua regia, which evolves chlorine.

(18) The bromine oxidizes Fe, As, and Sb to Fe(III) , As(V) , and Sb(V) , which do not interfere in the titration.

(19) Complete extraction is indicated when only light, flocculent silica particles remain. These are easily distinguishable from the original dark, dense ore particles. If much unextracted residue remains at this point, it is given more drastic treatment (HClO_4 , or fusion with Na_2CO_3). Student samples do not require such treatment unless so directed by the instructor.

(20) The earlier fuming with H_2SO_4 makes treatment with urea unnecessary.

(21) For excellent work, the relative range of triplicates should be less than 0.3%, and the relative error of the mean should be less than 0.3% for most ores. The principal sources of error are incomplete extraction and losses by spattering during the extraction process. Certain artificial and easily opened samples may be analyzed at the 0.1% error level.

QUESTIONS

Section 20A

1. Give reasons why each one of the following reductants and oxidants is unsatisfactory for use in standard solutions. (a) Dilute HNO_3 , (b) conc. H_2SO_4 , (c) oxygen, (d) H_2O_2 , (e) HClO_4 , (f) H_2S , (g) bromine.

2. Explain why Ag is a better reducer in 1 M HCl than in 1 M H_2SO_4 or 1 M HClO_4 .

3. Explain why an aqueous solution of a very strong reducer would be inherently unstable, and give an example. Repeat the explanation for a very strong oxidizer.

4. Write balanced equations for each of the following preoxidations or pre-reductions.

- | | |
|---|---|
| (a) $\text{Cr}_2\text{O}_3 + \text{Na}_2\text{O}_2$, in fusion | (e) TiO^{2+} in the Zn reductor |
| (b) $\text{Cr}_2\text{O}_3 + \text{Na}_2\text{O}_2$, in alkaline solution | (f) Fe^{3+} in the Ag reductor |
| (c) $\text{Mn}^{2+} + \text{S}_2\text{O}_8^{2-}$ in acid solution, Ag^+ catalyst | (g) $\text{NO}_3^- + \text{Devarda's alloy}$ |
| (d) $\text{H}_2\text{S} + \text{HClO}_4$ (hot, conc.) | (h) $\text{SO}_2 + \text{Fe}^{3+}$ in acid solution |
| | (i) VO_2^+ in the Zn reductor |

Section 20B

1. For which titration would the titration curve show the sharpest end point, Ce(IV) with Fe(II) or Fe(III) with Sn(II) ?

2. Which potentiometric titration curve is steeper, NaCl against AgNO_3 , or NaI against AgNO_3 ?

3. As Fe(II) is oxidized in a titration, how does the E change? How does the voltage of a Pt electrode in the titrated solution change when measured against a normal calomel electrode?

4. Distinguish between an internal redox indicator and an internal specific indicator. Give examples.

5. What is meant by the reversibility of an indicator? Is reversibility a necessary property of an indicator?

6. Distinguish between the transition range and transition potential of an indicator.

7. Show diagrammatically (as in Fig. 20.2, p. 447) how to follow the titration of (a) AgNO_3 with standard NaCl ; (b) FeSO_4 with standard KMnO_4 ; (c) HCl with standard NaOH ; (d) KI with standard KIO_3 .

8. Design a cell in which the reaction of Fig. 20.2 occurs without direct contact between the reagents. Explain how the ions migrate through the bridge.

9. Explain how a KI-starch solution might be used as a redox indicator in titrating a reducing agent (A_{red}) with an oxidizing agent (B_{ox}). Explain clearly what requirements must be met for the KI-starch to be a satisfactory indicator.

Section 20C

1. Permanganate reacts slowly with H_3AsO_3 in HCl , but not stoichiometrically according to the equation on page 455. Speculate as to what might be the side reactions.

2. What happens to the oxidizing titer of a KMnO_4 solution if the KMnO_4 decomposes to MnO_2 , which settles out?

3. From the acid ionization constants of H_3AsO_3 , in what form would it exist predominantly at $\text{pH } 10$? At $\text{pH } 14$?

4. What is autocatalysis? Compare it with ordinary catalysis.

5. In the autocatalyzed titration of $\text{H}_2\text{C}_2\text{O}_4$, standard KMnO_4 is added in 1-ml increments. Give roughly the shape of the curve that shows how the rate of reaction after addition of each increment depends on the total volume of KMnO_4 added.

6. Write the balanced equations outlining one of the determinations of Table 20.3A (p. 456). Repeat for Table 20.3B.

7. Write the equation for the reaction of KMnO_4 on $\text{K}_3\text{Co}(\text{NO}_2)_6$ (Table 20.3). Show that there are 11 eq per mole of the cobaltinitrate.

8. Can FeSO_4 be determined permanganometrically in the presence of KBr ? Devise a method of analyzing a solution containing these two substances.

Section 20D

1. Explain why the color of the starch-iodide-iodine complex is destroyed by alkalis.

2. Explain how the presence of HgCl_2 would interfere with the starch end point.

3. A thiosulfate solution could be standardized with I_2 , $\text{K}_2\text{Cr}_2\text{O}_7$, KIO_3 , $\text{K}_3\text{Fe}(\text{CN})_6$, Cu , or KMnO_4 . Give the number of equivalents per mole for each of these substances.

4. Using chemical equilibria, explain why iodine would be lost much more rapidly by volatilization from 0.0010 M I_2 in water than from 0.0010 M I_2 in 0.10 M KI .

5. In the presence of HgCl_2 , iodine oxidizes H_3AsO_3 even in acid solution. Explain.

6. Write balanced equations to show formation of the products of the air-oxidation of $\text{Na}_2\text{S}_2\text{O}_3$.

7. Why should $\text{Na}_2\text{S}_2\text{O}_3$ not be titrated against acid KMnO_4 solution? What might be some of the products?

8. If a standard $\text{Na}_2\text{S}_2\text{O}_3$ solution decomposes as on page 464, how does the normality with respect to reaction with iodine change if the SO_2 remains dissolved in the solution?

9. If $\text{Na}_2\text{S}_2\text{O}_3$ is unstable in acid solution, why may iodine be titrated with thio-sulfate in 3-4 *N* acid solutions, and what are the precautions necessary to prevent error?

10. Explain why the iodine titer of an $\text{Na}_2\text{S}_2\text{O}_3$ solution decreases on aging in air.

11. Titration of H_3AsO_3 and of $\text{Na}_2\text{S}_2\text{O}_3$ with standard iodine should each be performed in neutral or very weakly acid solutions, but for different reasons. State and compare these reasons.

12. What is the sign of the error if there is air-oxidation of the KI in standardizing $\text{Na}_2\text{S}_2\text{O}_3$ with $\text{K}_2\text{Cr}_2\text{O}_7$?

13. Write equations outlining one of the determinations in Table 20.4A (p. 467). Repeat for Tables 20.4B and 20.4C.

14. Speculate on the mechanism by which Cu_2I_2 acts as a catalyst in the determination of Fe(III), as outlined in Table 20.4B.

15. Outline an iodimetric method of analysis for a sample containing H_3AsO_3 , H_3AsO_4 , and inert material.

16. Why must buffers sometimes be used in the direct titration of oxidizers with standard iodine solutions? Name some appropriate buffers.

17. An acid solution contains $\text{K}_2\text{Cr}_2\text{O}_7$ and FeCl_3 . How would the solution have to be treated in order to determine the $\text{K}_2\text{Cr}_2\text{O}_7$ iodimetrically?

Section 20E

1. Since there are no stable oxidation states except Ce(III) and Ce(IV), is it correct to infer that intermediate and side reactions cannot destroy the stoichiometry of titrations with Ce(IV) solutions? Give specific examples to support your answer.

2. In 1 *M* HF, Ce(IV) does not oxidize KI. Explain.

3. Why is Ce(IV) often called "cerate," as well as "ceric"?

4. After extended heating in aqueous solution, the titer of Ce(IV) standard solutions decreases. What might be an equation for the decomposition?

5. In the determination of thiosulfate with cerate, use chemical equations to explain what is meant in Table 20.5A (p. 471) by the statement, "KI is both catalyst and indicator."

6. Write balanced equations outlining a determination in Table 20.5A. Repeat for Table 20.5B.

7. Describe the error caused by the presence of fluoride in the titration of an FeSO_4 solution with standard Ce(IV) in H_2SO_4 , with ferroin as an indicator.

Section 20F

1. Describe how you would establish the equivalence point in the titration of a sample containing Fe(II) with standard Mo(III). What would you expect might be some of the disadvantages in this titration?

2. In the determination of ferrous ion in a tartaric acid solution containing excess H_2SO_4 , explain which would be the better titrant, ceric sulfate or $\text{K}_2\text{Cr}_2\text{O}_7$.

3. If they were present during titration of an FeSO_4 sample with standard $\text{K}_2\text{Cr}_2\text{O}_7$, which of the following substances would interfere: Sn(II), Sn(IV), H_3PO_4 , H_2SO_4 , HgCl_2 , $\text{K}_3\text{Fe}(\text{CN})_6$?

4. In the preoxidation of Cr with Na_2O_2 , what would happen if the Na_2O_2 were not completely destroyed before acidification of the solution?

5. With the help of the TSP, explain why preoxidation of Cr with peroxide is performed in basic solution rather than in acid solution.

6. Write equations for preoxidation of Cr^{3+} to $\text{Cr}_2\text{O}_7^{2-}$ with the following pre-oxidants: $\text{K}_2\text{S}_2\text{O}_8$, HClO_4 , PbO_2 , KMnO_4 . Describe how the excess of preoxidant is removed in each case before titration of the dichromate.

7. Generally, when is it more advantageous to determine an element by titration of its oxidized form with a standard reducing solution, rather than by titration of its reduced form with a standard oxidizing agent?

Experiment 20.1 (Fe in an ore)

1. Why does the SnCl_2 reagent solution contain so much HCl?

2. Give the effect of each of the following mistakes on the measured Fe content of an ore, when SnCl_2 is the prereducer and $\text{K}_2\text{Cr}_2\text{O}_7$ is the titrant. (a) A large excess of SnCl_2 is added in prereducing the sample solution. (b) HgCl_2 is not added before titration of the prereduced ore sample. (c) The Fe titer of the $\text{K}_2\text{Cr}_2\text{O}_7$ is erroneously low. (d) The primary standard normality for the $\text{K}_2\text{Cr}_2\text{O}_7$ is used instead of the Fe titer. (e) In the standardization, the prereduced solution is left to stand overnight before titration.

3. Speculate as to why the normality of $\text{K}_2\text{Cr}_2\text{O}_7$ calculated from the Fe titer value is higher than the primary standard value.

4. Suppose that SnCl_2 is used to speed extraction of Fe from the ore, as described in Note 18 (p. 481). Explain the nature of the error caused by the presence of Sn, if an Ag reductor is used for prereduction instead of SnCl_2 .

5. Write balanced equations for each of the following processes. (a) Air-oxidation of Fe(II). (b) The reaction of Hg_2Cl_2 in causing a fading end point when Ce(IV) or KMnO_4 is the titrant. (c) Slow reduction of Fe(III) by metallic Hg in HCl solution.

6. Write balanced equations for the behavior of TiO^{2+} , of $\text{Cr}_2\text{O}_7^{2-}$, and of VO_2^+ upon addition of excess (a) Zn, (b) SnCl_2 , (c) Ag in 1 M HCl.

Experiment 20.2 (Ca in limestone)

1. What sorts of processes may occur to change the titer of a KMnO_4 solution in storage?

2. Explain why standard $\text{Na}_2\text{C}_2\text{O}_4$ solution is less stable in soft glass than in Pyrex or polyethylene bottles.

3. Suppose that the CaC_2O_4 were precipitated by adjusting the solution to pH 7.0 with NH_3 and then adding $\text{Na}_2\text{C}_2\text{O}_4$ to throw down the CaC_2O_4 . Describe the nature and contamination of a CaC_2O_4 precipitate so obtained and the direction of the error.

4. Using chemical equations, describe what happens to each of the following impurities, if present in the original sample: SiO_2 , Fe_2O_3 , Al_2O_3 , MgCO_3 , P (as $\text{Ca}_3(\text{PO}_4)_2$).

5. Although the blanks called for in this determination are easy to determine, they do not compensate for several possible sources of determinate error. List these sources. Outline a procedure for standardization and/or analysis which would minimize these errors more efficiently than does the blank correction.

6. Compare the solubility products of CaSO_4 and CaC_2O_4 . Explain why CaSO_4 is formed from CaC_2O_4 in this determination.

7. Describe the effect, if any, of each of the following mistakes on the measured CaO content of the sample. (a) The sample is dried at red heat before being weighed

out. (b) Coprecipitated oxalates are not completely washed away from the CaC_2O_4 . (c) The CaC_2O_4 is washed with too much water. (d) Silica coprecipitates with the CaC_2O_4 . (e) The KMnO_4 normality is erroneously high. (f) The CaC_2O_4 is dissolved in 4 *M* HCl instead of in H_2SO_4 . (g) All titrations (in standardization and sample analysis) are done by the McBride method. (h) The sample is not ignited. (i) The CaC_2O_4 is allowed to stand in its mother liquor overnight before being filtered. (j) The blank determinations are not performed.

Experiment 20.3 (Cu in an ore)

1. An $\text{Na}_2\text{S}_2\text{O}_3$ solution turns milky a few days after preparation. Write the equation for the reaction which has occurred. What may have been done incorrectly in the preparation?

2. Rewrite the equations for the iodimetric determination of Cu more correctly, representing iodine as triiodide.

3. Explain how addition of NH_4HF_2 forms a buffer solution.

4. Why does the end point fade if the solution is too basic?

5. If a blank were determined, explain how it could be either positive or negative.

6. Describe the effect of each of the following mistakes in analyzing an ore sample for Cu. (a) N oxides are not removed from the ore sample solution. (b) Too much NH_3 is added, giving the blue Cu(II)-NH_3 complex. (c) Only 0.2 g of NH_4HF_2 is added. (d) Insufficient KI is added. (e) After KI is added, the solution is left overnight before titration. (f) KSCN is not added. (g) Starch indicator is added early in the titration. (h) The volume of $\text{Na}_2\text{S}_2\text{O}_3$ is read as 27.02 instead of correctly as 28.02 ml. (i) The $\text{Na}_2\text{S}_2\text{O}_3$ is standardized immediately after preparation, and then used to titrate a sample several weeks later without being restandardized.

7. Explain the following phenomena: (a) If insufficient NH_4HF_2 is added in a Cu ore analysis, the solution may turn red just before the end point, after addition of KSCN . (b) The solution turns from deep blue to greenish after addition of NH_4HF_2 in analysis of a Cu ore.

8. Write balanced equations for: (a) Action of bromine in dissolving the S formed in extraction of the ore with HNO_3 . (b) Oxidation of H_3AsO_3 by bromine. (c) Action of hot conc. HClO_4 on CuS . (d) Action of hot conc. HNO_3 during extraction on H_3AsO_3 , if present. (e) Dissolution of Fe(OH)_3 by NH_4HF_2 . (f) Action of small and large amounts of NH_3 on Cu(II) . (g) Action of HF on glass.

PROBLEMS

Section 20B

1. Show that the E of the titrated solution in Fig. 20.1 (p. 442) is equal to E_{Fe}° at the half-way point. At what point in the titration is E equal to E_{Ce}° ?

2. Check the E values in Fig. 20.1 for the following volumes: 0.50, 5.00, 49.00, 49.90, 49.99, 50.05, 50.50, 55.00 ml.

3. Compute $[\text{Fe}^{3+}]/[\text{Fe}^{2+}]$ for the points listed in Prob. 2, and annotate on Fig. 20.1.

Ans. 5.0×10^2 at 49.90 ml.

4. Construct a titration curve for one of the following titrations, using 0.1000 *M* solutions. (a) Fe^{3+} with Sn^{2+} . (b) $\text{Cr}_2\text{O}_7^{2-}$ with Sn^{2+} . (c) H_3AsO_3 with Ce^{4+} . (d) TiO^{2+} with Cr^{2+} . (Assume that $[\text{H}^+]$ is 1.00 *M* for all points in the titrations.)

5. In Exs. 1 and 2, pages 443–45, calculate the E 's from the Ce^{4+} and Ce^{3+} concentrations, showing them to be identical to the values calculated from the Fe^{3+} and Fe^{2+} concentrations.

6. Calculate the equivalence-point E for one of the following titrations. Assume

$[H^+] = 1.00\ M$ at the equivalence points. Also, express the equivalence-point E with respect to the normal calomel electrode. (a) $0.100\ N\ FeCl_2$ with $0.100\ N\ KMnO_4$. (b) $0.100\ M\ SnCl_2$ with $0.0500\ M\ H_3AsO_4$. *Ans.* (a) 1.39, 1.11 v.

7. For one of the titrations of Probs. 4 or 6, calculate the change in E on passing from 0.1% before to 0.1% after the equivalence point, and select a suitable redox indicator. *Ans.* (4a) 0.594 to 0.24 v, methylene blue; (6a) 0.948 to 1.47 v, ferroin.

8. If diphenylamine sulfonic acid is used as an indicator for the titration represented by Fig. 20.1, calculate the % Fe remaining in the reduced state at the transition potential ($pH\ 0$). Repeat the calculation for ferroin in $0.5\ M\ H_2SO_4$.

9. What must be the E° of a half-reaction if at least 99.8% of the substance is to exist in the oxidized state at the transition potential of diphenylamine sulfonic acid? Assume that the half-reaction is of the $Fe^{3+}-Fe^{2+}$ type. *Ans.* 0.69 v.

10. What should be the transition potential of an indicator suitable for the titration of $0.100\ M\ FeCl_3$ with $0.100\ M\ TiCl_3$, if $[H^+] = 0.100\ M$ at the equivalence point?

11. Convert Fig. 16.2 (p. 277) to a potentiometric titration curve, resealing the vertical axis in terms of the E of an Ag electrode immersed in the titrated solution.

Ans. E is 0.50 v when pAg is 5.00.

12. For each of the following titrations, diagram an electrochemical cell with which the equivalence point may be found potentiometrically. (Use a saturated calomel reference electrode.) Calculate the equivalence-point voltage. On the diagram, and at the equivalence point, show: the electrode polarities, the direction in which electrons flow in the external circuit, the direction in which cations flow in the bridge, and the electrode reactions that occur when current is allowed to flow in the cell.

(a) A 50.00-ml portion of $0.05000\ M\ SnCl_2$, titrated with $0.01000\ M\ KMnO_4$. (Assume that $[H^+]$ is $1.00\ M$ at the equivalence point.)

(b) A 50.00-ml aliquot of $0.2000\ M\ H_3AsO_3$, titrated with $0.1000\ M\ K_2Cr_2O_7$. (Assume that $[H^+]$ is $1.00\ M$ at the equivalence point.)

(c) A 50.00-ml portion of a solution containing $0.1500\ M\ K_4Fe(CN)_6$, titrated with $0.0800\ M\ Ce(SO_4)_2$ in $1.0\ M\ H_2SO_4$.

(d) A 20.00-ml portion of $0.2500\ M\ AgNO_3$, titrated with $0.1000\ M\ KCl$. (Assume that the reference electrode bridge contains KNO_3 instead of KCl , so that the titrated solution does not become contaminated with chloride.)

Ans. (a) 0.87 v. Calomel electrode is negative. Electrons flow from calomel to platinum electrode. Cations migrate from calomel to platinum electrode.

At platinum (cathode), $Sn^{4+} + 2e \rightarrow Sn^{2+}$; at calomel (anode), $2Hg_{(l)} + 2Cl^- \rightarrow Hg_2Cl_2 + 2e$.

13. A 0.435-g sample of an Fe ore is leached with HCl , and the iron is prereduced with a slight excess of $SnCl_2$. Without removal of the excess $SnCl_2$, the solution is titrated potentiometrically with $0.1000\ N\ Ce(SO_4)_2$, Pt and saturated calomel electrodes being used. From the following pairs of volume and voltage readings, plot the titration curve and calculate the Fe content of the ore as % Fe_2O_3 . 0.00 ml (initial reading), 190 mv; 2.50, 230; 3.00, 240; 3.20, 250; 3.40, 267; 3.60, 300; 3.80, 315; 4.00, 325; 34.00, 515; 34.50, 538; 35.00, 570; 35.50, 625; 35.80, 700; 36.00, 910; 36.20, 1050; 36.50, 1095; 37.00, 1120. *Ans.* 59.7%.

Section 20C

1. What is the size of the blank when $0.01\ N\ KMnO_4$ is used in titration, assuming that the end-point volume of the titrated solution is 200 ml? *Ans.* 0.200 ml.

2. One drop (0.05 ml) of 0.002 M KIO_3 is required to catalyze the permanganate-arsenite reaction. Considering that the iodate ends as ICl at the equivalence point, calculate the error caused by the addition of KIO_3 , expressing this error as an equivalent volume of 0.1 N $KMnO_4$.

3. What is the As_2O_3 titer of a $KMnO_4$ solution whose Fe titer is 6.95 mg/ml?

Ans. 6.17 mg/ml.

4. What is the equivalent weight of Pb_3O_4 , when determined in an ore by the method of Table 20.3B (p. 456)?

5. When determined as in Table 20.3, give the titer values of 0.1500 M $KMnO_4$ in terms of : Fe_2O_3 , U_3O_8 , KNO_2 , SnO_2 , $K_2Cr_2O_7$, V_2O_5 (prereduced with Zn), Pb_3O_4 .

Ans. 105.2 mg U_3O_8 /ml.

6. A 0.3000-g portion of $Na_2C_2O_4$ requires 27.00 ml of $KMnO_4$ for titration. How many milligrams of As_2O_3 are in a sample which requires 49.20 ml of the $KMnO_4$ for titration?

7. An x -g sample of $Na_2C_2O_4$ requires for titration y ml of $KMnO_4$. What is the normality of the $KMnO_4$?

Ans. $14.925x/y N$.

8. A solution contains KHC_2O_4 . If 25.00 ml of this solution require 32.52 ml of 0.1057 N $KMnO_4$ for a redox titration, how many milliliters of 0.1293 N base would be required for the titration of 35.00 ml of the KHC_2O_4 solution? What would be the answer to this question if the original solution had contained $KHC_2O_4 \cdot H_2C_2O_4$?

9. How many milligrams of Mo are in a sample which requires 27.43 ml of 0.2000 N $KMnO_4$ for titration by the method of Table 20.3A?

Ans. 175.4 mg.

10. A 4.00-g sample of a U ore requires 30.76 ml of 0.1500 N $KMnO_4$ by the method of Table 20.3A. What is the U content of the ore, as % UO_3 ?

11. A 4.00-g sample contains only $Na_2S_2O_8$ and Na_2SO_4 . After acidification and addition of 50.00 ml of 0.1000 N $FeSO_4$, the excess $FeSO_4$ requires for titration 27.93 ml of 0.0500 N $KMnO_4$. What is the % $Na_2S_2O_8$ in the sample (Table 20.3B)?

Ans. 10.73%.

12. A 1.000-g sample of steel is dissolved and treated to convert all P to phosphate, which is then determined as in Table 20.3B. What is the % P in the steel, if 29.65 ml of 0.1600 N $KMnO_4$ are required for titration?

13. The Fe and Ti in a 0.4000-g sample of an ore are isolated as the hydrous oxides and redissolved in acid to give 250.0 ml of solution. A 100.0-ml aliquot, after passage through the Zn reductor, requires 18.37 ml of 0.1000 N $KMnO_4$ for titration. Another 100.0-ml aliquot, after prereduction with SO_2 , requires 9.73 ml of 0.1000 N $KMnO_4$ for titration. What are the percentages of TiO_2 and Fe_2O_3 in the sample?

Ans. 43.1, 48.6%.

14. An Fe ore contains 0.28% Ti. In an analysis for Fe, the sample is prereduced in a Zn reductor and then titrated with standard $KMnO_4$. If the analyst does not realize that Ti is present, and if he reports it as Fe, what is the error in the reported % Fe?

15. By mistake, a student uses $Na_2C_2O_4$ to standardize a $KMnO_4$ solution, thinking that he is using $H_2C_2O_4 \cdot 2H_2O$. He calculates that the $KMnO_4$ is 0.1056 N , and uses this solution to determine the Fe content of an ore as 55.6% Fe_2O_3 . Calculate the correct % Fe_2O_3 in the ore.

Ans. 52.3%.

16. A 3.17-g sample of a manganese steel is dissolved in HNO_3 . On the addition of $KClO_3$ to the hot solution, MnO_2 precipitates quantitatively and is filtered off. The precipitate is dissolved in a solution containing H_2SO_4 and 50.00 ml of 0.1000 N $FeSO_4$. Titration of the solution requires 4.61 ml of 0.1000 N $KMnO_4$. Calculate the % Mn in the steel (see Table 20.3B).

17. A sample of steel weighs 1.900 g and contains 0.66% Mn. After it is dissolved and the Mn preoxidized to permanganate, excess 0.1000 *N* FeSO₄ is added. If titration of the excess FeSO₄ requires 18.35 ml of 0.2000 *N* KMnO₄, how many milliliters of standard FeSO₄ were added? *Ans.* 48 ml.

18. A 10.00-ml aliquot of dilute H₂O₂ solution (density, 1.010 g/ml) requires 40.50 ml of 0.1107 *N* KMnO₄ for titration. Calculate the molarity and weight percentage of H₂O₂ in the solution.

19. A 2.000-g sample containing FeSO₄ and Fe₂(SO₄)₃ is dissolved in boiled dilute H₂SO₄ and made up to 250.0 ml. A 50.00-ml aliquot requires 32.93 ml of 0.09625 *N* KMnO₄ for titration. Another 50.00-ml aliquot, after prereduction with a Zn reductor, requires 47.26 ml of the KMnO₄. Calculate the percentages of Fe(II) and Fe(III) in the sample. *Ans.* 44.25, 19.26%.

20. A 3.50-g sample containing only Na₃AsO₃, Na₂CO₃, and NaCl requires 38.76 ml of 0.2000 *M* HCl for titration to the methyl orange (*pH* 4) end point. After addition of excess acid, the solution requires 21.63 ml of 0.1500 *N* KMnO₄ for titration. Calculate the composition of the sample.

21. A 10.00-ml aliquot of solution containing HI and HCl requires 45.70 ml of 0.2000 *N* NaOH for neutralization, and 36.35 ml of 0.2500 *N* KMnO₄ for titration. Calculate the molarity of each acid in the aliquot.

Ans. 0.4544 *M* HI and 0.4596 *M* HCl.

22. A 2.00-g mixture of Ag and Ag₂O is added to an excess of 0.2 *M* Fe₂(SO₄)₃ in 0.5 *M* H₂SO₄. The resulting solution requires 41.53 ml of 0.2000 *N* KMnO₄ for titration. Calculate the composition of the mixture. Outline the method with balanced equations, and explain carefully the function of the Fe₂(SO₄)₃.

23. Calculate the equilibrium constant for the reaction between Mn²⁺ and MnO₄⁻ in acid solution. In the light of the answer, explain how a sufficient excess of MnO₄⁻ can be built up to perceive the end-point color in a permanganimetric titration.

Ans. 1.6×10^{47} .

24. Calculate the equilibrium constant for the decomposition of MnO₄⁻ in slightly acid solution:



What is the equilibrium pressure of oxygen over a solution containing 0.0010 *M* KMnO₄, if [H⁺] = 1.0 *M*? Discuss the answers.

Section 20D

1. When determined as in Table 20.4A (p. 467), give the titer values of 0.0800 *N* iodine in terms of: Sb₂O₅, SnO₂, SO₂. *Ans.* 2.562 mg SO₂/ml.

2. When determined as in Table 20.4, give the titer values of 0.0900 *N* Na₂S₂O₃ in terms of: K₂Cr₂O₇, KIO₃, Ca(OCl)₂, K₃Fe(CN)₆, BaCO₃, CdS.

Ans. 4.413 mg K₂Cr₂O₇/ml.

3. What volume of 0.10 *N* iodine is required to give a blue color with starch, in 100 ml of a solution containing 10⁻³ *M* KI? (This is an estimate of the starch indicator blank.) *Ans.* 0.0002 ml.

4. The solubility of iodine in water at 25°C is 0.00134 *M*, and the predominant equilibrium is I_{2(s)} ⇌ I₂. What would be the molar solubility of iodine in 0.100 *M* KI, using the value of 7.1 × 10² as the equilibrium constant for triiodide formation?

5. A solution contains 2.00 g Na₂SO₃ and 9.62 g Na₂S₂O₃ per liter. What is its normality with respect to iodine? What is the iodine titer?

Ans. 0.0926 *N*; 11.75 g/l.

6. After the addition of excess KI to a 25.00-ml portion of 0.1000 *N* Ce(SO₄)₂, 49.32 ml of Na₂S₂O₃ solution are required for titration. What is the normality of the Na₂S₂O₃?

7. Suggest a range of sample weights for an ore containing 30–50% Sb, if 25–50 ml of 0.1000 *N* iodine is to be used for titration. *Ans.* 0.51–0.61 g.

8. A 50.00-ml portion of a solution of hydrazine (N₂H₄) in H₂SO₄ requires 46.23 ml of 0.1000 *N* standard iodine solution for titration. Calculate the molarity of the hydrazine solution. How many milligrams of N₂H₄ are in the portion?

9. A 2.00-g sample of an ore, after removal of interferences and conversion of all Sb to H₃SbO₃, requires 22.97 ml of 0.1000 *N* iodine for titration. What is the Sb content, as % Sb₂O₃? *Ans.* 8.37%.

10. Excesses of KI and H₂SO₄ are added to a 0.6000-g sample containing only KCl and KClO₃. If titration with 0.05000 *N* Na₂S₂O₃ requires 29.91 ml, what is the % KClO₃ in the sample?

11. Calculate the milligrams of H₂S per liter of an air sample from the following data: A 50.0-l sample of air is bubbled through an ammoniacal CdCl₂ solution, precipitating CdS. The CdS is dissolved in an acid solution containing 50.00 ml of 0.1000 *N* iodine solution. Titration of the excess iodine requires 12.97 ml of 0.1500 *N* Na₂S₂O₃ solution. *Ans.* 1.041 mg/l.

12. Sn in a 3.00-g sample is determined iodimetrically as outlined in Table 20.4A. Calculate the Sn content as % SnO₂, if 26.25 ml of a standard iodine solution (titer, 1.03 mg As₂O₃ per milliliter) are required for titration.

13. A 0.2500-g sample containing 55.0% KNO₂ and 45.0% KCl is dissolved and added to an excess of acidified KI. How much 0.1000 *N* Na₂S₂O₃ is required for titration? *Ans.* 16.16 ml.

14. Excesses of KI and HCl are added to a KIO₃-KCl sample. If 41.02 ml of 0.1000 *N* Na₂S₂O₃ are required for titration by the method of Table 20.4B, what is the weight of KIO₃ in the sample?

15. A 2.230-g sample of bleaching powder is dissolved and made up to volume in a 250-ml volumetric flask. A 25.00-ml aliquot requires 33.02 ml of 0.1158 *N* Na₂S₂O₃ for titration by the method of Table 20.4B. Calculate the percentage of "available chlorine" in the bleaching powder. Calculate the Ca(OCl)₂ content, assuming that this compound is the sole oxidant in the bleaching powder.

Ans. 60.8% chlorine; 61.3% Ca(OCl)₂.

16. A 0.5500-g sample of a Pb ore is dissolved and the Pb is precipitated quantitatively as PbCrO₄. After the PbCrO₄ is dissolved in acid and excess KI is added, 47.60 ml of 0.1000 *N* Na₂S₂O₃ are required for titration. Express the Pb content as % PbS.

17. In an indirect volumetric method for sulfate determination, an excess of BaCrO₄ is added to the sample solution. The SO₄²⁻ metathesizes BaCrO₄ to BaSO₄, one mole of CrO₄²⁻ being put into solution for each mole of SO₄²⁻ originally present in the sample. The precipitate is removed by filtration. The filtrate is acidified, treated with excess KI, and titrated with standard Na₂S₂O₃. What is the Na₂SO₄ molarity of a solution, a 25.00-ml portion of which requires 33.21 ml of 0.1387 *N* Na₂S₂O₃ for titration? (In order to avoid error, the determination entails details not given above. Speculate as to what might be the principal sources of error, and check with the literature (M6).) *Ans.* 0.0614 *M*.

18. The oxygen in an organic compound may be determined iodimetrically by the Unterzaucher method (U9). The oxygen in the compound is converted quantitatively by pyrolysis over carbon to CO, which in turn is passed over I₂O₅ to liberate iodine.



What is the percentage of oxygen in a 0.2276-g sample which requires 29.23 ml of 0.1000 *N* $\text{Na}_2\text{S}_2\text{O}_3$ for titration of the collected iodine?

19. In the determination of aldehydes by the method of Table 20.4C, the excess HSO_3^- is titrated with standard iodine solution in the presence of the addition compound. The equilibrium constant for the formation of the benzaldehyde-bisulfite addition compound is 1.0×10^4 .

(a) Calculate the concentration of excess HSO_3^- that must be present so that no more than 0.10% of the benzaldehyde is present in the uncombined form.

(b) If the rate of dissociation of the addition compound were appreciable during the iodimetric titration, what would be the effect?

(c) A 0.7000-g sample of impure benzaldehyde ($\text{C}_6\text{H}_5\text{CHO}$) is placed in a 100-ml volumetric flask. Then 50.00 ml of 0.2500 *M* NaHSO_3 are added, the contents diluted to the mark, and 5 minutes are allowed for complete reaction. A 25.00-ml aliquot requires 31.45 ml of 0.1000 *N* iodine for titration. Calculate the per cent of benzaldehyde in the preparation. *Ans.* (c) 94.2%.

20. An excess of KI is added to 0.01000 *M* $\text{Fe}_2(\text{SO}_4)_3$, so that at equilibrium, $[\text{I}^-] = 1.00$ *M*. What is the concentration of unreduced Fe^{3+} at equilibrium? Discuss the feasibility of determining Fe(III) iodimetrically.

21. A 25.00-ml portion of a solution contains FeCl_2 and FeCl_3 . It is treated with excess citrate, which complexes Fe(III) so that it cannot oxidize I^- . A 25.00-ml portion of 0.1000 *N* iodine is added, and the excess is titrated with 0.1000 *N* $\text{Na}_2\text{S}_2\text{O}_3$, 6.28 ml being required. Next, the solution is acidified with 5 *N* HCl , which destroys the Fe(III)-citrate complex. After addition of an excess of KI, titration of the iodine formed requires 47.81 ml of 0.1000 *N* $\text{Na}_2\text{S}_2\text{O}_3$. Calculate the concentrations of FeCl_2 and FeCl_3 in the original solution.

Ans. 0.0749 *M* FeCl_2 ; 0.1164 *M* FeCl_3 .

Section 20E

1. (a) If all U is in the form of U_3O_8 in a sample, and if the U is determined as outlined in Table 20.5A (p. 471), what is the equivalent weight of U_3O_8 ? Repeat for (b) Fe as FeS , (c) Cr as NaCrO_2 , (d) Te as Te , (e) Sn as SnS_2 , (f) Ca as CaO , (g) P as P_2O_5 , (h) Na as Na_2SiO_3 , (i) K as KCl . *Ans.* (a) 140.348.

2. What is the titer value of 0.1000 *N* $\text{Ce}(\text{SO}_4)_2$, in terms of each of the substances whose equivalent weights are sought in Prob. 1? *Ans.* (a) 14.03 mg $\text{U}_3\text{O}_8/\text{ml}$.

3. What is the normality of a cerate solution, 42.6 ml of which are required to titrate a 0.2952-g sample of $\text{Na}_2\text{C}_2\text{O}_4$? *Ans.* 0.1033 *N*.

4. The K in a 0.6000-g sample containing only KCl and NaCl is determined as in Table 20.5B. What is the % KCl , if 36.52 ml of 0.1200 *N* cerate are required for titration?

5. A 1.000-g sample containing only Ag metal and Ag_2O is treated with an excess of $\text{H}_2\text{SO}_4\text{-Fe}_2(\text{SO}_4)_3$ solution. The Fe(II) formed requires 27.26 ml of 0.1063 *N* cerate for titration. What is the % metallic Ag in the sample? Explain the function of the $\text{Fe}_2(\text{SO}_4)_3$. *Ans.* 31.26%.

6. What is the percentage of KI in a KI-KCl sample, 0.500 g of which requires 38.96 ml of 0.1250 *N* $\text{Ce}(\text{SO}_4)_2$ to titrate to ICl by the method of Table 20.5A?

7. The Cr in a 0.2000-g mineral sample is extracted and determined as in Table 20.5B. If 50.00 ml of 0.1000 *N* $\text{Ce}(\text{SO}_4)_2$ are added originally, and if 6.52 ml of 0.1000 *N* KNO_2 are used to titrate the excess cerate, what is the % Cr_2O_3 in the mineral? *Ans.* 55.1%.

8. The H_3AsO_3 -cerate titration is carried out in an end-point volume of 200 ml, with a concentration of ICl catalyst at 1.0×10^{-4} *M*. If the iodine catalyst is added as KI instead of ICl , what would be the blank, in terms of 0.100 *N* cerate?

Section 20F

1. What is the molarity of a $K_2Cr_2O_7$ solution having a titer of 39.6 mg Fe_2O_3 per ml?
Ans. 0.0828 *M*.
2. Give the titers of a 0.01690 *M* $K_2Cr_2O_7$ solution in terms of Fe_2O_3 and Cr_2O_3 .
3. A 2.000-g sample of an ore, after extraction and prereduction of Fe, requires 36.25 ml of 0.1265 *N* $K_2Cr_2O_7$ for titration. What is the Fe content as % Fe_3O_4 ?
Ans. 17.70%.
4. A 50.00-ml portion of 0.1000 *N* $FeSO_4$ is added to a 1.800-g sample of a Cr ore after extraction, preoxidation of the Cr, and removal of interferences. Back titration of the excess $Fe(II)$ requires 5.82 ml of 0.1300 *N* $K_2Cr_2O_7$. Express the Cr content of the ore as % Cr_2O_3 .
5. Equal weights of $K_2Cr_2O_7$ and K_2CrO_4 are dissolved, each in 1 l of solution. What is the ratio of the normalities?
Ans. 1.3202.
6. A 1.023-g sample of an Fe ore is dissolved and prereduced. It is overtitrated with 46.61 ml of 0.1123 *N* $K_2Cr_2O_7$, and 1.87 ml of 0.1000 *N* $FeSO_4$ is used in back titration. What is the Fe content of the ore, as % FeS_2 ?
7. A 0.250-g sample of a chromite ore is fused with Na_2O_2 to convert Cr_2O_3 to Na_2CrO_4 . The melt is then dissolved and the excess Na_2O_2 is destroyed. The solution is acidified and titrated with standard 0.1000 *N* $FeSO_4$ solution, 20.72 ml being required. What is the Cr content of the ore, as % Cr_2O_3 ?
Ans. 21.0%.
8. A 0.3000-g sample of an Mn steel is dissolved in conc. HNO_3 and Mn is oxidized to permanganate with excess $(NH_4)_2S_2O_8$. The excess persulfate is destroyed by boiling, leaving permanganate as the only oxidizing agent in the solution. A 50.00-ml portion of 0.0911 *N* $FeSO_4$ is then added. The excess $FeSO_4$ is back-titrated with 0.0907 *N* $K_2Cr_2O_7$, 4.26 ml being required. What is the % Mn in the steel?

Experiment 20.1 (Fe in an ore)

1. After prereduction, 50.00 ml of an $FeCl_3$ solution require 29.25 ml of a $K_2Cr_2O_7$ solution for titration. If the $FeCl_3$ solution contains 10.000 g of Fe per liter, what is the normality of the $K_2Cr_2O_7$ solution? The Fe titer?
Ans. 0.3061 *N*; 17.09 mg/ml.
2. A 0.2650-g sample of Fe wire is dissolved and prereduced. How many milliliters of 0.1500 *N* $K_2Cr_2O_7$ are required for titration?
3. How many milliliters of 0.1000 *N* $K_2Cr_2O_7$ could be prepared from 3.652 g of primary standard $K_2Cr_2O_7$?
Ans. 745 ml.
4. An Fe ore contains 40–50% Fe_3O_4 . What range of sample sizes may be used in order that 25–50 ml of 0.1000 *N* $K_2Cr_2O_7$ will be required for titration?
5. Calculate the percentage of Fe_2O_3 in an ore, a 0.673-g sample of which requires 29.76 ml of 0.1000 *N* $K_2Cr_2O_7$ for titration.
Ans. 35.3%.
6. Repeat Prob. 5 if instead of being 0.1000 *N* the dichromate has an Fe titer of 5.123 mg/ml.
7. Calculate the equilibrium constant for the reaction



Use the answer to explain why a chloride medium is essential for the determination of Fe as performed in Exp. 20.1.
Ans. 1.1×10^5 .

8. Calculate the equilibrium constant for the reaction



Use the answer to explain why the Ag reductor must be used in chloride medium in order to reduce Fe^{3+} quantitatively.

Experiment 20.2 (Ca in limestone)

1. The Ca content of a limestone is 26.25% CaO. What volume of 0.1234 N KMnO_4 would be required for titration of a 0.3670-g sample? *Ans.* 27.84 ml.

2. A limestone sample contains 30–40% CaO. What range of sample sizes may be used in order that 30–50 ml of 0.1000 N KMnO_4 will be required for titration?

3. If a 2.842-g sample of limestone requires 42.1 ml of 0.1009 N KMnO_4 for titration, what is the Ca content of the ore, as % CaO? As % CaCO_3 ? *Ans.* 41.9%; 74.8%.

4. In Prob. 3, what weight of CaC_2O_4 would be obtained during the analysis?

5. Calculate the equilibrium constant for the reaction



What is the solubility of CaC_2O_4 in a solution of a strong acid, such as HClO_4 , in which $[\text{H}^+] = 0.100 M$? (Hint: Formation of HC_2O_4^- is not negligible.)

Ans. 5.4×10^{-4} ; 0.0029 M .

6. Calculate the equilibrium constant for the reaction



What is the solubility of CaC_2O_4 in a sulfuric acid solution, in which $[\text{H}^+]$ is 0.100 M and $[\text{SO}_4^{2-}]$ is 0.050 M at equilibrium? Compare answers with Prob. 5.

Experiment 20.3 (Cu in an ore)

1. What is the Cu titer of an $\text{Na}_2\text{S}_2\text{O}_3$ solution, if 39.23 ml are required to titrate 0.2396 g of Cu? What is the normality? What assumptions are made in calculating the normality? *Ans.* 6.108 mg/ml; 0.09612 N .

2. What is the CuCO_3 titer (in mg/ml) of a 0.1500 N $\text{Na}_2\text{S}_2\text{O}_3$ solution?

3. A sample may contain 18–20% CuO. What range of sample sizes may be taken, in order that 25–45 ml of 0.1000 N $\text{Na}_2\text{S}_2\text{O}_3$ may be used for titration?

Ans. 1.1–1.8 g.

4. The Cu content of an ore is 14.26% CuCO_3 . What volume of 0.1526 N $\text{Na}_2\text{S}_2\text{O}_3$ is required to titrate a 1.000-g sample?

5. If 19.26 ml of 0.0500 N $\text{Na}_2\text{S}_2\text{O}_3$ are required to titrate a 1.500-g sample of a Cu ore, what is the Cu content, as % CuS? *Ans.* 6.14%.

6. How many milliliters of $n N$ $\text{Na}_2\text{S}_2\text{O}_3$ would be required to titrate w g of Cu?

7. According to the half-reactions listed in the TSP of Appendix IX, there is no indication that Cu^{2+} will oxidize I^- . However, CuI is insoluble, and its solubility product may be found in Appendix V.

(a) Calculate E° for the half-reaction



(b) Calculate the equilibrium constant for the reaction



(c) What fraction of the total Cu remains unreduced when 30.0 ml of 0.100 M KI are added to 20.0 ml of 0.0250 M CuSO_4 ? *Ans.* (a) 0.860 v.

21 SPECTROPHOTOMETRY

21A. INTRODUCTION

21A.1. Properties of Light and Electromagnetic Energy

21A.1a. Physical properties. Light is a form of radiant or electromagnetic energy, propagated with a wave motion. All kinds of electromagnetic energy are propagated with the same *velocity*, 3.00×10^{10} cm/sec in vacuum. Different kinds of electromagnetic energy are characterized by the *wavelength* (λ), or *frequency* (ν),* related by the equation

$$(\lambda, \text{ in cm})(\nu, \text{ in sec}^{-1}) = 3.00 \times 10^{10} \quad (21.1)$$

Electromagnetic energy also has a particulate nature, the *energy* (E) of each particle (i.e., *quantum* or *photon*) being related to its frequency by Einstein's equation.

$$(E, \text{ in ergs}) = 6.6 \times 10^{-27} (\nu, \text{ in sec}^{-1}) \quad (21.2)$$

Figure 21.1 shows the various regions of the electromagnetic spectrum. *Light* is the name given to those wavelengths of electromagnetic radiation that are directly perceptible by the human eye. It may be seen that the visible region corresponds to a very small portion of the whole spectrum.

*The wavelength is the distance between crests of the wave motion, while the frequency is the number of waves passing a given point per unit of time. It follows that the product is the velocity with which the wave motion is propagated.

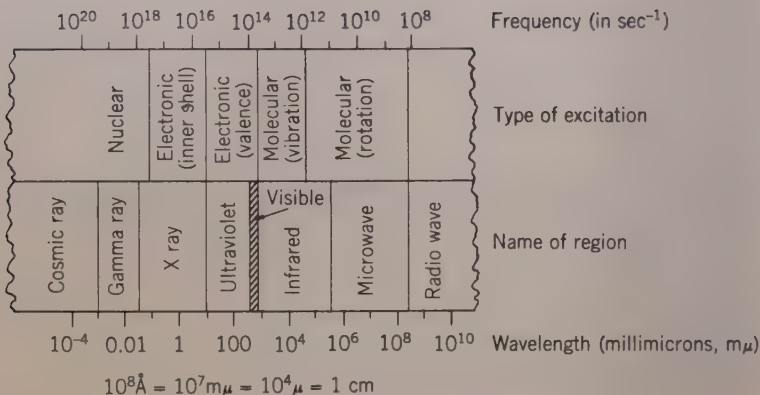


FIG. 21.1. The Electromagnetic Energy Spectrum

A beam of radiation is characterized not only by its wavelength, but also by its *intensity*, which is proportional to the number of quanta per second propagated in the beam. A beam carrying radiation of only one wavelength is said to be *monochromatic*, while a *polychromatic* beam contains radiation of several wavelengths.

21A.1b. Absorption of electromagnetic energy. All students are familiar with the absorption of heat by matter, and how the heat energy goes to increase the energy (i.e., velocity) of the molecules in the absorbing material. Electromagnetic energy is also capable of being absorbed by matter, but when absorbed, it goes principally to increase the energies of the electrons and atoms within the molecules of the absorbing material.*

The electrons within an atom and the atoms within a molecule are in continuous motion, each vibrating at definite natural frequencies corresponding to definite energy states which are specifically characteristic of the atomic and molecular structure. If radiation of a frequency (i.e., energy) corresponding to one of the natural frequencies strikes an atom or molecule, the radiant energy may be absorbed to increase the energy of the atom or molecule. Radiation that does not correspond to one of the natural frequencies is not absorbed. The electronic and atomic configuration of any substance is a highly specific property of the atomic and molecular structure; thus, the frequency range within

*At best, this is the primary step in the mechanism of absorption. It should be recognized, however, that the electrons and atoms cannot remain long in their energized or excited states, and that their surplus energies are immediately dissipated within the bulk of the absorbing material, most often as heat, but sometimes initiating chemical reactions and sometimes being reemitted as light.

which absorption occurs is specifically dependent upon the nature of the absorbing material. No two substances absorb identically over the whole electromagnetic spectrum.

The energy of a quantum of exciting light increases with frequency (i.e., increases with decreasing wavelength). The nature of the changes brought about by the radiation therefore depends on the wavelength. Visible and ultraviolet light is energetic enough to energize the loosely bound outer (valence) electrons. Infrared radiation is not energetic enough to excite electrons, and can only increase the rotational and vibrational energy of the atoms in the absorbing molecules. On the other hand, X rays can excite the tightly bound inner electrons, and gamma and cosmic rays can bring about nuclear transformations. Figure 21.1 summarizes the types of excitation that may be brought about by various types of radiation.

21A.1c. Visual properties of light. Color. Visible light consists of that narrow portion of the electromagnetic spectrum to which the human eye is sensitive. Visible radiations lie in the range from $380\text{ m}\mu$ (a radiation that provides a violet stimulus to the eye) to $780\text{ m}\mu$ (which provides a red stimulus to the eye). Figure 21.2 shows an enlargement of the visible region, with the colors corresponding to various wavelengths.



FIG. 21.2. The Visible Region of the Spectrum

If the eye is stimulated by light containing all wavelengths of the visible region, the effect is that of white light; the sensation of color results if wavelengths from one or more portions of the visible region are appreciably absent. As far as the eye is concerned, light has three properties—hue (or color), color intensity, and brightness. The *hue* or *color* is determined by the proportions of the different wavelengths present. If light of a certain color or wavelength is removed from white light, the resultant color is the complementary one shown in Table 21.1. The *color intensity* of a given hue is determined by the proportion of that hue to the proportion of white light in the beam. If the proportion of a given hue is high, the color intensity is high, and the color is described as “vivid” or “intense.” If the proportion of a given hue is low, the color intensity is low, and the color is described as “pale” or “weak.” Color intensity bears no simple relation to the intensity meas-

ured with a photocell. The *brightness* of a light beam is determined by the total radiant power in the beam. The light from the noonday sun is classed as very "bright," while that from the clear night sky is classed as "dim" or "dark." All these properties are important in colorimetry, where the eye is used as the detector, but are of little consequence in spectrophotometry.

As examples of the use of this terminology, the following statements are made with the aid of Table 21.1. If wavelengths in the blue region are rather completely removed from white light, the resultant light is a vivid or intense yellow, while if the blue wavelengths are only partially removed, the resultant light is a pale or weak yellow. As another example, if green light is removed or absorbed from white light, the residual light is purple in hue, the color intensity of the purple being dependent upon the extent to which the green is removed.

TABLE 21.1
RELATION BETWEEN ABSORPTION AND COLOR*

Wavelength Region Removed by Absorption (m μ)	Color Absorbed	Complementary Color of the Residual Light, as Seen by the Eye
400-435.....	violet	yellow-green
435-480.....	blue	yellow
480-490.....	green-blue	orange
490-500.....	blue-green	red
500-560.....	green	purple
560-580.....	yellow-green	violet
580-595.....	yellow	blue
595-650.....	orange	green-blue
650-750.....	red	blue-green

*Reprinted from C. R. Noller, *Chemistry of Organic Compounds*, 2d ed. (Philadelphia: Saunders, 1957), Table 28, by permission of the publisher.

21A.2. Spectrophotometry in Chemical Analysis

21A.2a. Definition and scope. *Absorption spectroscopy* and *spectrophotometry* are the names given loosely to those methods by which substances are identified or measured through their absorption of electromagnetic radiation. Such measurements are of great analytical use—both qualitatively and quantitatively. Since the wavelengths at which a substance absorbs are so specifically dependent upon the nature of the absorbing molecules, absorption spectroscopy may be used to identify the absorbing substance and to elucidate its structure. Also, as will be shown later, the extent of absorption at any particular wave-

length may be taken as a measure of the concentration of the absorbing substance.

Spectrophotometric procedures are not restricted to colored sought-for substances that absorb in the visible region of the spectrum, for many colorless substances absorb in the nonvisible spectral regions. There are methods for both identification and determination of substances in the X-ray, ultraviolet, infrared, and radio-frequency regions of the spectrum, each region having its own unique advantages and applications. However, the visible region is the most accessible one, with the simplest equipment, and the remainder of this chapter is concerned almost exclusively with it.

Spectrophotometric procedures involve a nice balancing of chemistry and physics. The theory and techniques of measuring light fall within the field of physics, but the preparation of the solution and the development of the color involve chemical principles and techniques. The chief limitations of most spectrophotometric procedures lie in the chemical reactions upon which these procedures are based rather than in the instruments available. Modern instruments fulfill the needs of the analyst fairly well.

21A.2b. Spectrophotometric methods compared with gravimetric and volumetric methods. With the rapid advances in instrumentation that began in the thirties, spectrophotometric methods have enjoyed a steady rise in popularity. (See p. 13.) The increase in popularity will probably continue as the recently discovered magnetic resonance techniques of the microwave region find increased application to chemical problems.

Advantages of spectrophotometric methods. (1) In general, spectrophotometric methods are simpler and more rapid than gravimetric or volumetric ones. (2) Some substances are very intensely colored, and give perceptible absorption at trace concentrations. Spectrophotometric methods may therefore be used on the microscale, where ordinary gravimetric or volumetric procedures fail entirely. With conventional equipment, it is not uncommon to determine some substances spectrophotometrically at concentrations down to $10^{-7} M$, in volumes of only a few milliliters. With microchemical techniques and equipment, spectrophotometric methods are extendable into the ultramicro regions. Such methods are of especial use in clinical analysis. (3) Spectrophotometric procedures are often much more specific than volumetric or gravimetric ones. This follows from the inherent specificity of the absorption process, and also from the comparative ease with which colors of sought-for or interfering substances may be developed or altered by chemical reaction. (4) Spectrophotometric reactions need not be stoichiometrical or complete, although they must satisfy other requirements (p. 524).

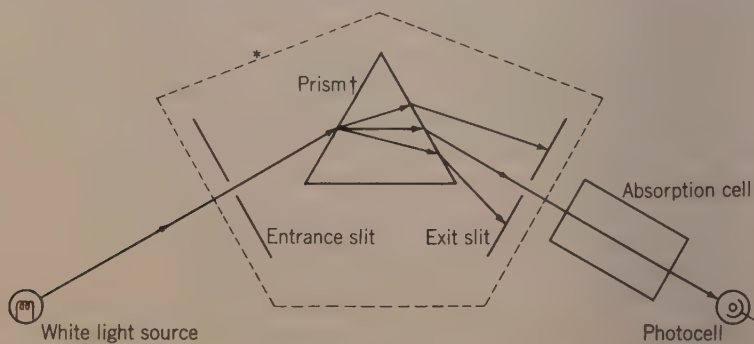
Disadvantages of spectrophotometric methods. (1) The relative errors obtained with spectrophotometers range from a few tenths of a per cent to several per cent. To keep errors to the lower ends of these ranges requires both experience and good instruments. The errors of spectrophotometric procedures, in short, generally fall at the 1% level, rather than the 0.1% level. For many applications in industrial control, trace analyses, and biochemical analyses, this is not a limitation at all, for relative errors of 1% are easily tolerable. (2) From the very nature of the measurements, most spectrophotometric determinations are not stoichiometric but empirical. Ultimately, every unknown sample is analyzed by comparison with a standard solution of the sought-for substance. While this is again not a severe disadvantage, it must be admitted that such empirical procedures are not so desirable as stoichiometrical ones, which do not require calibration.

21B. SPECTROPHOTOMETRIC ANALYSIS

21B.1. Outline of the Spectrophotometric Method

According to the restricted definition of the analyst, a spectrophotometric determination is one in which the sought-for substance is estimated by noting its light absorption within a rather narrow wavelength range. Restriction of the wavelength generally gives greater sensitivity and selectivity than can be obtained when the wavelength is unrestricted.

The measurement is performed with a *spectrophotometer*, which may have the elements shown in Fig. 21.3. Each of the elements is described in greater detail in the Supplement (p. 867).



*The assemblage within the dotted lines is called the monochromator.

†Prism rotates to make any desired wavelength region fall upon the exit slit.

FIG. 21.3. Elements of a Spectrophotometer

In practice, the absorption of a solution is measured at a particular wavelength by noting how the photocell response with the absorption cell filled with solution compares with the response when the absorption cell contains a nonabsorbing solution.

21B.2. Light Absorption by Solutions

21B.2a. Beer's law. Let light of intensity I_o be incident upon a solution that contains a concentration, C , of an absorbing substance. After the light has traversed the solution for a distance, b , the intensity is reduced to I . These quantities are related by *Beer's law*.

$$\log \frac{I}{I_o} = -abC, \quad \text{or} \quad \frac{I}{I_o} = 10^{-abC} \quad (21.3)$$

Beer's law is fundamental in spectrophotometry; it is the basis for estimating the concentration of a substance by measuring the light absorbed by a solution of that substance. The derivation of Eq. 21.3 is given in the Supplement (p. 869).

The quantities in Eq. 21.3 must be discussed from the viewpoint of practical use. The ratio I/I_o is called the *transmittance*, and is a dimensionless ratio, since I and I_o are expressed in the same units. The combination abC , being a logarithm, must also be a pure number, and it is essential that the units of each quantity be carefully specified. Much confusion arises from failure to do so. When C is expressed in molar units and b in centimeters, then a has the units, $(\text{moles/l})^{-1}(\text{cm})^{-1}$, and is called the *molar absorptivity*. The *absorptivity*, a , is given other special names when it possesses other dimensions. The absorptivity is characteristic of the absorbing substance.

Example 1. The molar absorptivity of a solute is 2.10×10^4 . Find the transmittance through a 0.50-cm thickness of a $2.00 \times 10^{-5} M$ solution.

$$\log \frac{I}{I_o} = -abC = -(2.10 \times 10^4)(0.50)(2.00 \times 10^{-5}) = -0.210$$

$$\frac{I}{I_o} = 10^{-0.210} = 10^{-1+0.790} = 0.617, \text{ or } 61.7\%$$

Example 2. The intensity of a light beam is halved on traversing a 1.00-cm thickness of absorbing medium. What thickness must be traversed to reduce the emergent intensity to (a) one-fourth, (b) one-tenth of the incident intensity?

(a) If traversing 1.00 cm halves the intensity, another 1.00 cm will halve it again, or reduce the intensity to one-fourth of the incident intensity. *Ans.* 2.00 cm.

(b) Using the reasoning of part a, it may be seen that a length of 3–4 cm is needed. More rigorously, the proportionality constant between $\log I$ and b may be found.

$$\log \frac{I_o/2}{I_o} = -a(1.00)C$$

$$aC = -\log \left(\frac{1}{2}\right) = \log 2 = 0.301$$

From the value of aC , the length required for a tenfold reduction of intensity may be found.

$$\log \frac{I}{I_o} = -abC$$

$$\log \frac{I_o/10}{I_o} = -0.301b$$

$$b = -\frac{\log 0.1}{0.301} = 3.32 \text{ cm}$$

21B.2b. Transmittance curves. When transmittance (I/I_o) is plotted against wavelength for a given sample of absorbing solution (C and b in Eq. 21.3 being constant), the resulting curve is called a *spectral transmittance curve*. The value of I/I_o varies with wavelength (i.e., the absorptivity varies with wavelength) in a way characteristic of the absorbing substance and the solvent in which it is placed.

Figure 21.5 (p. 529) gives some typical transmittance curves for aqueous inorganic solutions. Some substances have very discrete curves, with many peaks. Some samples of didymium glass have ten distinguishable peaks between 400 and 700 $m\mu$, and are used to calibrate wavelength scales on spectrophotometers. Organic substances usually have more complicated transmittance curves than inorganic ones. Spectra in the infrared region are highly discrete, and are therefore very useful for qualitative and quantitative analysis.

The shape of a transmittance curve is dependent to some extent upon the characteristics of the spectrophotometer used to measure the curve. Thus if the instrument does not allow selection of sufficiently narrow wavelength regions, fine detail in the transmittance curve may be incompletely resolved or may even be obliterated. An example is the single minimum shown in the absorption curve for KMnO_4 (curve A, Fig. 21.5). When measured with a spectrophotometer of high resolving power, a double minimum is found to exist around 525 $m\mu$.

There are other ways of expressing the ratio of incident to transmitted intensities. The ratio I_o/I is a measure of absorption, and plots of I_o/I against wavelength are called *absorption curves*. $\log I_o/I$ is called the *absorbance* or *optical density*. In certain applications, the measurement and use of absorbance is favored over transmittance (p. 514).

21B.2c. Limitations of Beer's law. Beer's law (Eq. 21.3) is correct, as far as it goes, in describing the relationship between I/I_o , C , and b .

However, it should not be inferred that C and b are the *only* variables affecting I/I_0 . On the contrary, I/I_0 for a particular sample in a particular cell is dependent upon many other factors. It is important to recognize and to control these factors, for if they change, variations are introduced into I/I_0 , and Beer's law appears to break down.

Beer's law is said to be an ideal, or limiting, law, to which there are no exceptions.* If in a real case any exceptions are noted, these exceptions are not interpreted to disprove the validity of the law, but are "explained" as variations in one or more of the following factors.

Wavelength. Although not explicitly stated in Eq. 21.3, it was explained above that the absorptivity, a , and therefore the transmittance of a particular sample is highly dependent upon wavelength. The relationship of Eq. 21.3 applies only to strictly monochromatic light; it is valid for a wavelength interval only when a is constant throughout that interval. If there is more than one wavelength present in the incident light, and if the absorbing substance shows different values of a for the different wavelengths, then there is an apparent failure of Beer's law as far as the total intensity transmitted by the sample over all the wavelengths is concerned. (Proof of this failure is given in the Supplement, p. 871.)

Light transmitted by mechanisms other than absorption. Any light which reaches the detector by a process other than absorption within the defined wavelength range may cause an apparent failure of Beer's law. Such failure may be caused in several ways: (1) Stray light which enters the detector by paths other than the path through the entrance and exit slits is potentially a source of great error. Careful design of instruments minimizes this error. (2) Reflected light, which traverses the absorbing medium more than once, will give deviation from Beer's law, for it is absorbed more effectively than that portion of the light that traverses the medium only once. (3) Scattered light from turbid samples, or emitted light from fluorescent samples, does not follow Beer's law, and may cause deviations.

Other absorbing species. Where there is more than one absorbing species, the relationship between I/I_0 and concentration must of necessity be more complicated than that indicated in Eq. 21.3. The case for two absorbing species is developed in the Supplement (p. 872).

Chemical effects. A number of kinds of chemical reactions may cause deviations from Beer's law, as described on page 520.

*Equation 21.3 is not an exact law; a is also dependent upon the refractive index, which in turn depends nonlinearly on concentration. However, the variation of refractive index with concentration is so slight as to be insignificant for almost all practical cases in spectrophotometric analysis (§2).

21B.3. Qualitative Analysis

Transmittance curves taken with the spectrophotometer are an excellent means of identification. A transmittance curve is a "signature" of the compound giving it. Identification of a component in this way is empirical, and is performed by searching in a library of transmittance curves of known compounds until a curve is found which agrees with that of the unknown compound. In making the identification, the important characteristics of the curve are the wavelengths and transmittances of the minima. (Further details are given in the Supplement, p. 875.)

21B.4. Quantitative Analysis

21B.4a. General method of spectrophotometric determination. Beer's law (Eq. 21.3) may be rewritten.

$$\log \frac{I_o}{I}, \text{ or } A = abC \quad (21.4)$$

The quantity $\log I_o/I$ is called the *absorbance*, A , and is directly proportional to concentration. In quantitative spectrophotometry, it is slightly more advantageous to measure absorbance than to measure transmittance, since logarithmic calculations are avoided. The scales of modern spectrophotometers are calibrated to read directly in both absorbance units and transmittance units.

The general procedure for a spectrophotometric determination is given below. It is suggested that Exp. 21.1 (p. 526) be studied as a specific and detailed example.

1. If it is not already known, the absorption spectrum of the sought-for substance should be found.
2. The working wavelength range is selected. There are many considerations affecting this selection. It is important to choose a wavelength range in which the sought-for substance absorbs, but in which other (interfering) substances that may be present do not. The method is then specific for the sought-for substance. By selecting the proper wavelength range, it is often possible to determine a sought-for substance in the presence of another differently colored substance—a determination that is impossible if the wavelength range is not restricted. A second consideration is that for maximum sensitivity a wavelength range should be chosen in which the sought-for substance shows high absorption. A third consideration, which is less important than the

first two, is that a should be substantially constant throughout the wavelength region employed. Then, other factors permitting, Beer's law is obeyed and the plot of A against C is a conveniently straight line. For these purposes, it is usually best to work at a minimum in the transmittance curve, and to restrict measurements to a narrow region of the spectrum. Mellon gives further considerations for the selection of the wavelength range (M14).

3. The working curve is established. The absorbances of several standard solutions with known concentrations of the sought-for substance are measured.* The plot of A (ordinates) against C (abscissae) is called the *working curve*. If the working curve is a straight line, Beer's law holds. If the working curve is not straight, Beer's law does not hold, but analyses can still be performed.

4. From the absorbance of the unknown solution, its concentration may be read directly from the working curve. For maximum precision, the sample size should be chosen so that the transmittance is neither very high nor very low (see Supplement, p. 876).

Example 1. Manganese in a steel sample may be determined by dissolving the sample in HNO_3 , oxidizing Mn to permanganate with KIO_4 , diluting to 250 ml, and measuring the absorbance of the resulting solution. Four standard steels and an unknown sample give the following data. Construct a working curve and find the % Mn in the unknown steel.

SAMPLE NUMBER	1	2	3	4	UNKNOWN
Per cent Mn.....	0.200	0.320	0.450	0.600	?
Weight of sample (g)....	0.550	0.512	0.487	0.502	0.491
Absorbance.....	0.236	0.351	0.467	0.644	0.398

For each standard steel, calculate the weight of Mn per milliliter in the solution whose transmittance is measured.

$$\left(\begin{array}{c} \text{For steel No. 1,} \\ \mu\text{g Mn per ml} \end{array} \right) = \frac{0.200 \times 10^{-2} \times 0.550 \times 10^6}{250} = 4.40 \mu\text{g/ml}$$

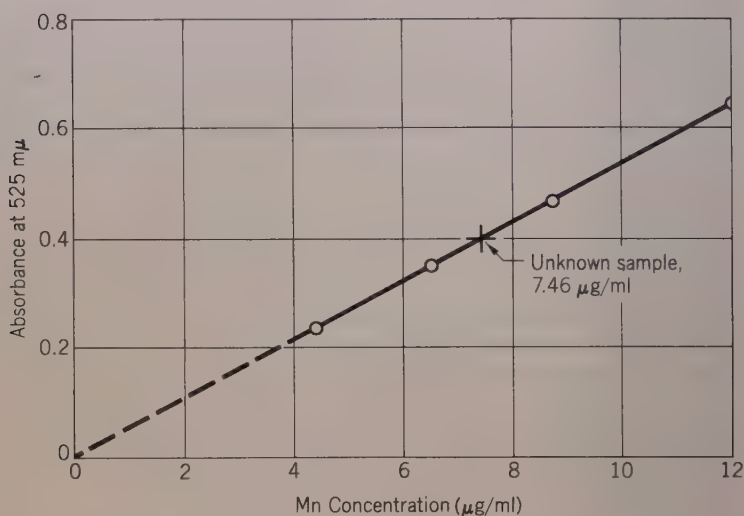
For steels Nos. 2, 3, and 4, respectively, the concentrations are 6.55, 8.77, and 12.05 $\mu\text{g Mn/ml}$.

Plot micrograms of Mn per milliliter as abscissae against absorbance as ordinates to obtain the working curve on page 516.

From the absorbance of the unknown steel solution, it may be found from the working curve that the solution contains 7.46 $\mu\text{g Mn/ml}$.

$$\left(\begin{array}{c} \% \text{ Mn in} \\ \text{unknown steel} \end{array} \right) = 7.46 \times 250 \times 10^{-6} \times \frac{100}{0.491} = 0.380\% \text{ Mn}$$

*Alternatively, transmittances may be measured and plotted. In this case, semilog graph paper is very convenient, since computation of logs is avoided.



Example 2. Assume that only the standard steel with 0.450% Mn and the unknown are measured in Ex. 1. Calculate the % Mn in the unknown, using Beer's law.

Let A_s and C_s refer to the standard steel solution, and let A_u and C_u refer to the unknown steel solution.

C_s may be calculated as 8.77 μg Mn/ml, as in Ex. 1.

Then

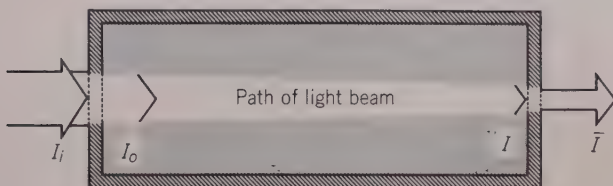
$$\frac{A_u}{A_s} = \frac{A_u C_s}{A_s C_u} \quad \text{or} \quad \frac{0.398}{0.467} = \frac{C_u}{8.77}$$

C_u is therefore 7.46 μg Mn/ml, from which the % Mn in the unknown steel may be calculated as in Ex. 1, to give the same answer.

Note: This procedure may be used only if it is known from prior experience that the working curve is straight, and if it intercepts the vertical axis at zero absorbance when extrapolated. Deviations from these requirements may cause considerable error, especially if the standard and unknown absorbances are considerably different. If it is not known that these requirements are satisfied, it is better to use a working curve, as in Ex. 1.

21B.4b. Practical measurement of transmittance. As defined in Beer's law, the transmittance is the ratio of the light intensity emergent from the sample to the incident intensity, I/I_o . For a spectrophotometric determination, the absolute values of I and I_o are not measured, since troublesome corrections would be required for intensity losses by reflection and absorption within the cell and the solution. Instead, the following procedure is used.

Let a cell that contains an absorbing solution be represented as follows:



I_i is the intensity incident upon the front face of the cell. \bar{I} is the intensity emergent from the cell, and is measured with a photocell. I_o and I , the intensities incident upon and emergent from the medium, as represented in Beer's law, are not directly measurable, and may be quite different from I_i and \bar{I} .

\bar{I} is directly proportional to I_i .

$$\bar{I} = I_i F_f F_s F_r (10^{-abC})$$

F_f , F_s , and F_r are the transmittances (i.e., the transmitted fractions of the incident intensity) of the front window, the pure solvent, and the rear window, respectively. For each of these media, F is less than unity because of losses by reflection and absorption. The differences from unity are appreciable; reflection losses alone are of the order of 5% per window for windows with plane surfaces, and may be much higher for cells with curved surfaces.

To measure a transmittance, \bar{I} is first measured for a cell containing a solution of the absorbing solute. Then, \bar{I} is measured for the same cell filled with pure solvent, in which case C is 0, 10^{-abC} is unity, and \bar{I} is symbolized by \bar{I}_o .

$$\bar{I}_o = I_i F_f F_s F_r \quad (\text{For pure solvent})$$

The ratio of \bar{I} to \bar{I}_o is

$$\frac{\bar{I}}{\bar{I}_o} = \frac{I_i F_f F_s F_r (10^{-abC})}{I_i F_f F_s F_r} = 10^{-abC}$$

This equation is identical with Beer's law; therefore, \bar{I}/\bar{I}_o must be identical to I/I_o . \bar{I}/\bar{I}_o is easy to measure, and it automatically corrects for losses within the cell and pure solvent.

A further simplification is possible. For all spectrophotometers, \bar{I} is obtained as a scale reading, as from the scale of a millimeter that measures the response of a photocell. By adjusting the sensitivity of the meter, \bar{I}_o can be made to read 100 units on the scale, and the scale

reading for \bar{I} then becomes the per cent transmittance. All commonly used spectrophotometers have this feature.

21B.4c. Sources of error and their minimization. If absorbance is taken as a measure of the concentration of an absorbing substance, then any factor other than concentration which affects absorption must be controlled. If the error-causing factor varies from the conditions selected for the determination, the sought-for concentration will be in error.

The magnitude of the resulting error depends upon (a) the magnitude of the variation in the error-causing factor, and (b) the sensitivity of the concentration to that variation. In making the error as small as possible, both of these properties should be utilized. For *a*, conditions should be selected to keep the magnitude of the variations at the minimum conveniently possible. For *b* it is important to keep the error-causing variable at a value for which the sought-for concentration is insensitive to changes in that variable. An example of such a selection to minimize instrumental scale-reading errors is given below.

1. *Instrumental errors.* When a working curve is established, it is obtained with a particular instrument, a particular cell, and a particular wavelength range. These conditions should be duplicated in the unknown determination. Even for the same make, individual instruments differ from each other (as regards slit-width settings, wavelength scales, stray light, cell dimensions, detector sensitivity, source intensity, etc.). All of these instrumental characteristics are potential sources of error, and might become operative if allowed to change between standard and unknown analyses. These errors are minimized by the use of the same equipment for standards and unknowns.

Not only should the same instrument be used, but even the external conditions (temperature, humidity, etc.) under which the instrument is used should not change between measurement of the unknown and the standard. In high resolution spectrophotometers, for example, temperature variations can cause changes in the wavelengths passed at a particular setting of the monochromator. Such instruments are used in air-conditioned rooms. Environmental changes are often unimportant if the sample and standard are measured within a short time. However, a working curve that is used over a long period of time for many analyses should be checked frequently, to ascertain that environmental errors have not crept in.

One instrumental error that is always present is the random error in reading the transmittance or absorbance scales. From the relationship between transmittance and concentration (Eq. 21.3), it may be seen that a small error in reading I/I_0 causes a large relative error in C , when I/I_0 is either small or large. For most instruments, the optimum

transmittance range is 20–60%, corresponding to an absorbance range of 0.2–0.7, and the sample size should be chosen to fall within this range (see Supplement, p. 880).

2. *Personal errors.* The most common personal errors in spectrophotometric analysis arise from the handling of equipment. The outside and inside of absorption cells must be kept scrupulously clean. Cells should be examined for scratches, fingerprints, and air bells not only before each measurement but also after. Solutions should be examined for light-scattering inhomogeneities, such as lint from towelling and undissolved particles of the sample.

Acceptable weighings, dilutions, and transfers usually require less care in spectrophotometric determinations at the 0.5–1% error level than in more precise gravimetric or volumetric analyses. Many of the ordinary sources of error in volumetric or gravimetric analyses are generally not important.

Gross computational errors are frequent, especially in the use of Beer's law and in dilutional computations.

3. *Impurities.* Errors due to impurities in distilled water and other reagents may be very serious, since many spectrophotometric methods operate at trace concentrations of the sought-for substance. Reagent-grade chemicals may have impurities inconsequential in ordinary volumetric or gravimetric methods but comparable to the amount of substance sought in a spectrophotometric analysis. The blank determination should always be made.

4. *Absorbing interferences.* If the sought-for component is the only one present which absorbs, its measurement is a comparatively simple affair. However, if there is present another substance which absorbs appreciably over the wavelength interval chosen for measurement of the sought-for substance, special precautions must be taken to avoid error.

The following chemical methods may be used to prevent error due to another absorbing substance. (a) The interfering substance may be removed from the system before the absorbance is measured. (b) Without removal from the system, the interfering substance may be changed by chemical reaction into a nonabsorbing form. The interference of Fe(III) in the determination of Mn as permanganate is prevented in this way by the addition of H_3PO_4 , which forms nonabsorbing ferric phosphate complexes (Note 9, p. 528). (c) If the absorption of the interfering substance cannot be altered, the sought-for substance may sometimes be changed by chemical reaction into a nonabsorbing form without altering the absorption of the interfering substance. Measurement of the absorbance before and after the change allows determination of the

sought-for substance. The determination of permanganate in the presence of dichromate may be made in this way (Note 16, p. 530).

If it is difficult or troublesome to eliminate absorbing interferences by the chemical methods described above, an alternative procedure is to make absorbance measurements at more than one wavelength, treating the system as a multicomponent one (p. 521).

5. *Chemical interferences.* It should be apparent that the absorbance must be stable and reproducible enough for measurement. If the absorbance is changed by any unsuspected or slow reaction, error may be introduced. If the change is rapid, the method is a poor one. If the change is slow, it may still be possible to obtain reproducible results, provided that technique is carefully standardized, with special attention paid to the time interval between the addition of reagents and the measurement of absorbance.

Interfering reactions may be of several kinds. The colored substance may react with the solvent medium (e.g., hydrolysis of a sought-for species, followed by slow precipitation), or it may react with a component of the air, or it may simply decompose. The rates of such reactions are sometimes increased by the temperature rise of the solution when it absorbs light. Also, some substances are unstable to light, which may cause photochemical change when absorbed.

Less apparent, but very important, are the effects of equilibria involving the sought-for substance. In an analysis the total concentration of the sought-for substance is usually desired. If the sought-for substance is distributed among several solute species in equilibrium with each other, and if one of these species is colored, then the concentration of the colored species is related to the total concentration of the sought-for substance. In such a case, I/I_0 is also related to, and may be taken as a measure of, the total concentration of the sought-for substance, provided that there is proper control of factors affecting the equilibria. The relation between the absorbance and the total concentration of the sought-for substance may or may not be linear. The same conclusions apply if more than one of the solute species is colored. (Two examples showing the relationship between the absorbance and the total concentration of an absorbing substance distributed among several equilibrium forms are given in the Supplement, p. 873.)

There are many examples of spectrophotometric determinations wherein the sought-for substance is distributed among more than one solute species. Thus, Cu(II) is spectrophotometrically determinable as its deep-blue complex with excess NH_3 . Several complexes are formed: $\text{Cu}(\text{NH}_3)_4^{2+}$, $\text{Cu}(\text{NH}_3)_3^{2+}$, and $\text{Cu}(\text{NH}_3)_2^{2+}$. Each of these complexes possesses a slightly different absorption spectrum than the others. The

working curve of absorbance against total Cu concentration is curved, but reproducible.

Acidity control may be very important in some determinations. If the sought-for species has acid or basic properties, the distribution of that species among the acid and basic forms is greatly dependent upon pH . For example, Cr(VI) exists principally as yellow CrO_4^{2-} in basic solutions, and as orange $Cr_2O_7^{2-}$ in acid solutions. The spectrophotometric determination of Cr(VI) must therefore be performed at a controlled pH . As another example, many metal ions may be determined spectrophotometrically by being converted to highly colored complex ions with weak organic acids. The efficiency with which these complexes are formed depends greatly upon acidity, and the determinations must therefore be made in buffered solutions at controlled pH .

The effect of the solvent upon the absorption spectrum may be explained by recognizing that any solute species is necessarily solvated. The absorption spectrum observed is not that characteristic of the solute alone, but that of the solvated solute. Thus the absorption spectrum of a solute may be different in different solvents. (Iodine is yellow in water and violet in CCl_4 .) Even within a particular solvent, there may exist several species with different degrees of solvation, and the relative concentrations of these may change upon dilution. For example, $CuCl_2$ exists in dilute solution as blue, hydrated $Cu(H_2O)_4^{2+}$ and hydrated Cl^- . In concentrated solution, however, Cl^- displaces H_2O from the coordination sphere of Cu(II), forming greenish complexes with the formula $Cu(H_2O)_n \cdot Cl_{4-n}^{n-2}$. Because of these complexes, even pure water solutions of $CuCl_2$ alone do not follow Beer's law.

To summarize, in a spectrophotometric determination, whenever the sought-for substance is distributed among several solute species in equilibrium with each other, it is very important to maintain constant all factors that affect the equilibrium, such as temperature, ionic strength, and concentrations of all reagent species except the sought-for one.

Sandell (S2, p. 108) gives an excellent tabular summary of methods by which various kinds of interferences may be minimized.

21B.4d. Analysis of mixtures of two absorbing substances. If it is not possible or convenient to separate two absorbing substances for individual measurement, it may be possible to measure each in the presence of the other. Ideally, if the absorption spectra of the two substances (A and B) are sufficiently different, it may be possible to select a wavelength, λ' , at which component A absorbs and component B does not (Fig. 21.4). Conversely, to measure B in the presence of A, a wavelength must be found at which A absorbs negligibly compared to B. (There is no such wavelength on Fig. 21.4.) This ideal case is seldom

encountered in practice. However, even when no region can be found in which just one component absorbs, it is still possible to determine both substances by making measurements at two wavelengths, such as λ_A and λ_B (see Supplement, p. 872).

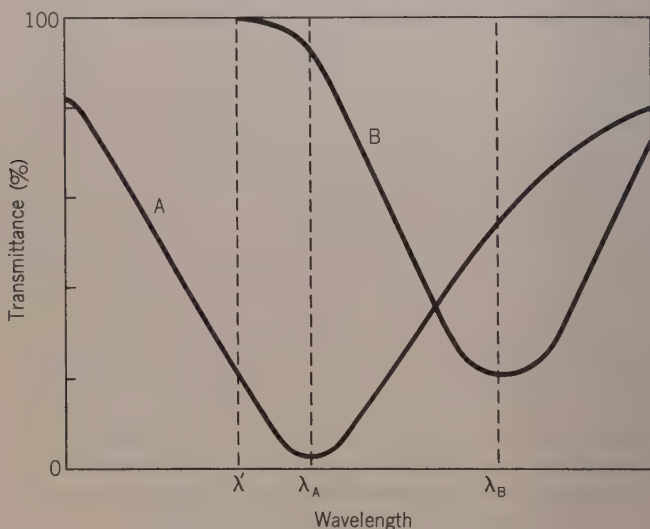


FIG. 21.4. Analysis of a Mixture of Two Absorbing Substances

21B.5. Filter Photometers

The *filter photometer* is an inexpensive spectrophotometer which isolates the desired portion of the spectrum with a filter (or filters) instead of with a grating or prism. Wavelength regions isolable by filters are not nearly so narrow as those isolable by good gratings or prisms, and therefore the selectivity of a filter photometer is not as high as that of a good spectrophotometer. This disadvantage is unimportant for many analyses that do not require high selectivity and narrow spectral bands. Because of the comparatively wide wavelength bands transmitted, the filter photometer operates at high intensities, and an inexpensive barrier-layer photocell may be used as a detector. A good description of filter photometers is given in Mellon's treatise (M14).

21C. THE CHEMISTRY OF SPECTROPHOTOMETRY

The conventional steps of the general analytical process (Chapter 2) are usually encountered before a spectrophotometric determination can be made. In addition, since so many spectrophotometric methods

operate at trace levels of the sought-for constituent, the techniques of trace analysis are often encountered. Particularly if the sought-for substance is present in the sample at a concentration too low for direct measurement, special methods must be used to concentrate the substance. Concentration methods include carrying by coprecipitation, solvent extraction, volatilization, and adsorption. Also, there is often the problem of separating the sought-for constituent at trace levels from a major amount of an interfering substance. Separation and concentration processes are discussed in advanced texts (M14, S2, Y2).

21C.1. Color Development

Only a few of the many elements that are spectrophotometrically measurable give sufficiently intense absorption by themselves. Instead, most substances are determined indirectly in a variety of ways: (1) The substance may be converted by a reagent to an absorbing product. For example, Fe(III) may be determined as its intensely colored complex with thiocyanate. (2) The sought-for substance may be made to react with an absorbing reagent. Thus, fluoride may be determined by its bleaching action on the color of the ferric thiocyanate complex; fluoride breaks up the colored ferric thiocyanate complex to form a very stable but colorless ferric fluoride complex. (3) The substance may be precipitated, the precipitate redissolved, and the precipitant associated with the sought-for substance may be determined spectrophotometrically. Mg and Al may be precipitated with 8-hydroxyquinoline (p. 570). After filtration and washing, the precipitate is dissolved in acid and the yellow 8-hydroxyquinoline is determined spectrophotometrically.

All types of chemical reactions are employed to develop color. (1) Redox reactions are occasionally used to bring an element to a colored valence state, or to produce a colored product. For example, Mn may be determined as permanganate after oxidation with periodate. (2) Organic reactions are used to convert organic substances to colored products for determination. Such reactions are often quite specific, and include diazotization and coupling, condensation, addition, and substitution. (3) Complexing reactions are used very frequently to form the absorbing complex. In some instances, the absorbing complex is inorganic (e.g., the red ferric thiocyanate complex, and the blue cupric ammonia complex). For the determination of metals, however, organic complexing reagents are by far the most sensitive and selective. The determination of Cu with dithizone is discussed in Sec. 21E. The theory and use of organic complexing reagents are given in more advanced texts (S2, W9).

21C.2. Desirable Properties of the Absorbing System

Among the characteristics desirable for an absorbing system are the following: (1) The system should be stable—at least sufficiently so to allow several checking measurements. There exist special techniques for the measurement of unstable systems (M14). (2) The color or absorption should be intense, for high sensitivity. (3) The absorption should not be critically dependent upon conditions such as pH, excess of reagents, or temperature. When there is such critical dependence, suitable control may be costly and troublesome. (4) Conformity to Beer's law is desirable, since procedure and calculation are simple when this law holds. Such conformity is not essential, however.

21C.3. Desirable Properties of the Color Developer

Among the characteristics desirable for the color-developing reagent are the following: (1) The reagent should be stable, so that solutions need not be prepared frequently. (2) The color-developing reaction should be rapid. (3) The reagent should react completely with the sought-for substance, according to a single, well-defined chemical equation. This is certainly not necessary, and many methods exist in which this requirement is not even approximately satisfied. In fact, for some methods, the nature of the absorbing product is not even known. However, when this requirement is satisfied there is a better chance that Beer's law will hold. (4) The reagent should be nonabsorbing—at least in the wavelength region where the sought-for color itself is measured. (5) The reagent should be selective.

21D. METHODS RELATED TO SPECTROPHOTOMETRY

There are some other methods of analysis that are generally grouped with spectrophotometric methods, because they involve the interaction of light with the sought-for substance, and because the equipment is much the same.

In a *turbidimetric* determination, the sought-for substance in solution is converted to a suspended precipitate, and a beam of light is passed through the suspension. The decrease in intensity of the transmitted beam is taken as a measure of the amount of sought-for substance (see Supplement, p. 882). A *nephelometric* determination is performed in the same way as a turbidimetric one, except that the intensity of the light scattered by the suspension is measured perpendicularly to the incident beam, and is taken as an indication of the amount of sought-for

substance (see Supplement, p. 884). In a *fluorimetric* determination, the sought-for substance is converted into a fluorescent compound, which gives off light when irradiated. The intensity of the fluorescent light is observed perpendicularly to the incident beam, and is taken as a measure of the amount of sought-for substance (see Supplement, p. 885). *Colorimetric*, or *color comparison*, procedures are still used, but not so widely as before spectrophotometric instrumentation became available (see Supplement, p. 888).

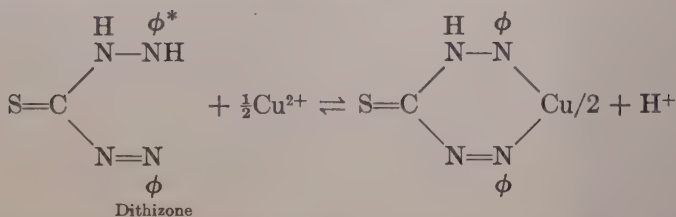
21E. EXAMPLES OF SPECTROPHOTOMETRIC PROCEDURES

Mellon's treatise (M14) contains an instructive classification of spectrophotometric procedures and a tabular summary of many methods for inorganic and organic substances. Working procedures for metals, nonmetals, and compounds of biochemical and clinical significance are gathered together in various works (A5, B20, S2). The following methods are outlined not because they are widely used, but rather because they illustrate the wide variety of spectrophotometric methods. Typical turbidimetric, nephelometric, fluorimetric, and colorimetric procedures are described in the Supplement (pp. 882–89).

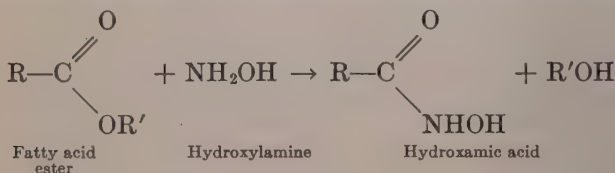
Determination of manganese as permanganate. Mn may be determined by oxidation to permanganate with a strong oxidizing agent, such as KIO_4 , PbO_2 , or NaBiO_3 (Exp. 21.1). The method is also used to determine small amounts of Mn in ores, in biological and plant materials, and in water (S21).

Determination of copper with dithizone. Dithizone forms a strongly colored complex with Cu(II) in acid solution, and the complex may be extracted with CCl_4 for measurement. The dithizone reagent itself absorbs, and there is no portion of the visible spectrum where either dithizone or its Cu complex absorbs negligibly. A two-color analysis is avoided, however, by the use of a constant amount of dithizone in all determinations. Measurement of the absorbance may be made at either 510 or 625 $\text{m}\mu$. At 510 $\text{m}\mu$, the complex has an absorption maximum, and absorbs more strongly than the dithizone, so that the absorbance increases as the Cu content of the sample increases. At 625 $\text{m}\mu$, the dithizone has an absorption maximum, and absorbs more strongly than the Cu complex, so that the absorbance decreases as the Cu content of the sample increases. With this method as little as 10^{-7} g of Cu may be determined with reasonable accuracy. At the proper pH the method is quite specific; only Pd, Au, Ag, Hg, and Bi interfere, and small amounts of some of these are tolerable.

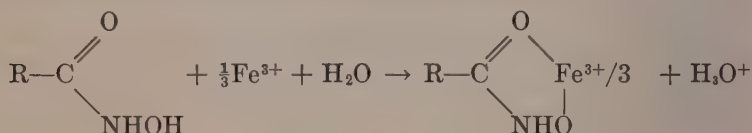
Dithizone is believed to complex Cu(II) as follows:



Determination of fatty acid esters. In alcohol-ether-NaOH medium, hydroxylamine converts fatty acid esters to hydroxamic acids:



After reaction, the solvents are driven off, and the mixture is acidified with an $\text{HClO}_4\text{-Fe}(\text{ClO}_4)_3$ solution, which gives a spectrophotometrically measurable red complex with the hydroxamic acid.



The method may be extended to fatty acids, after methylation with thionyl chloride and methanol in anhydrous ether solution.

EXPERIMENT 21.1. SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE IN STEEL

SUMMARY

The steel sample is dissolved in HNO_3 and the Mn is oxidized to permanganate with KIO_4 . The Mn content is determined with a spectrophotometer from the absorbance of the solution at $525 \text{ m}\mu$. Computations are made using Beer's law or a working curve. Interferences by Fe and Cr are discussed.

PROCEDURE

1. *Introduction.* Each student's time on the spectrophotometer is restricted to one half of a working period. The schedule is posted, and the student should plan his work in advance. It is recommended that

* ϕ symbolizes the phenyl group, C_6H_5 —.

the sample be checked out, dissolved, oxidized, and made up to volume during the period prior to the one scheduled for use of the instrument. Each student, when finished, must leave his working space and instrument in perfect condition. (See p. 139.) The pair of absorption cells accompanying the instrument must be left clean and dry. (Note 23.)

2. *Preparation of the standard steel solution.*

2a. Weigh 0.499–0.501 g of a standard steel sample into a 500-ml flask. (Notes 1–4.)

2b. Add 40 ml water and 10 ml conc. HNO_3 . After any violent bubbling subsides, boil gently for 2–3 minutes, to extract Mn completely from any slight residue that may remain. The whole dissolution procedure should be performed in a good hood. (Note 5.)

2c. Cool the solution below boiling, and slowly add about 1 g $(\text{NH}_4)_2\text{S}_2\text{O}_8$. (Note 6.) Boil the flask contents gently for 10 minutes to destroy the excess persulfate. (Notes 7, 8.)

2d. Dilute to about 100 ml with water, add 10 ml conc. H_3PO_4 , and then add 0.3–0.5 g KIO_4 . Boil the flask contents gently for about 3 minutes, swirling occasionally, until all KIO_4 crystals are dissolved. (Notes 9, 10.)

2e. Allow to cool below boiling, and add another 0.3–0.5-g portion of KIO_4 . Boil for 1 minute more. (Note 11.)

2f. Allow to cool, transfer quantitatively to the 250-ml volumetric flask, dilute to volume, and mix well. (Notes 12–14.)

3. *Preparation of the unknown steel solution.* Using a 0.499–0.501-g portion, prepare a solution of the unknown steel according to the procedure of step 2.

4. *Absorbance measurements.*

4a. Obtain instructions for operation of the spectrophotometer.

4b. After setting the instrument for zero absorbance with water as a reference solution, measure the absorbance of the standard steel solution at 525 $\text{m}\mu$. (Notes 15–19.) Repeat the setting of zero absorbance and the measurement of the sample absorbance until a reliable average is obtained. (Note 20.)

4c. Repeat step 4b for the unknown steel solution.

5. *Computations.* (Notes 21, 22.)

Method I. For a constant sample size, it follows from Beer's law that the absorbance is proportional to the % Mn in the sample, or

$$\frac{A_u}{A_s} = \frac{\% \text{ Mn in unknown steel}}{\% \text{ Mn in standard steel}}$$

Method II. If a group of four students works cooperatively, each student may prepare a different standard steel solution; then each will have at his disposal four standard solutions with which to prepare a

reliable working curve of absorbance against % Mn in the sample. Although the standard steel solutions may be used in common, each student should prepare his own working curve, using a particular instrument, a particular set of absorption cells, and his own techniques. The % Mn in each student's sample may then be found from its absorbance and that student's working curve.

NOTES

(1) There seems to be some interaction (nature unknown) between Fe(III) and permanganate, which affects the absorption of permanganate; the amount of Fe must therefore be roughly controlled by selecting a fixed sample size. Another advantage in the use of a precisely fixed sample size is that the absorbance then depends only on the % Mn, and computational effort is saved. (Compare the computations of step 5 with those of Exs. 1 and 2, page 515, where the sample size varies. Even though computations for variable sample size are unnecessary in this experiment, they should still be learned.)

(2) These directions are for steels containing 0.2–0.7% Mn. Other steels may require modification of procedure.

(3) Smaller sample sizes could be used, if dilutions were made to a smaller volume than the 250 ml of step 2f. This is not recommended, since the heterogeneity of metal alloys often requires the use of large samples to avoid sampling errors. It is also to avoid such sampling errors that powdered samples rather than coarse turnings are recommended for student use.

(4) If the sample is oily, rinse it with benzene and then acetone. Air-dry, and then oven-dry for 5–10 minutes at 100–110°C. (Never put articles wet with inflammable solvents into an oven.) Clean metal samples may be weighed out as received, without oven-drying.

(5) A slight amount of insoluble carbides, silicides, or silica may remain, and may be disregarded.

(6) Sprinkle the persulfate slowly into the hot solution to prevent violent frothing. The persulfate is an auxiliary oxidant, and is used to destroy as much reducing matter (organic materials, NO₂, etc.) as possible, so that only a minimum amount of the more expensive KIO₄ is required later. According to the TSP, persulfate is capable of oxidizing Mn to permanganate, but it does not do so under the conditions of this experiment (p. 823).

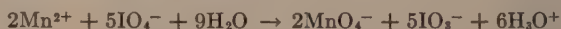
(7) The equation for the decomposition is



(8) Some of the Mn may precipitate as MnO₂ at this point, but no difficulty is caused, since the MnO₂ dissolves later upon oxidation to permanganate.

(9) Fe(III) absorbs appreciably at 525 mμ, where the permanganate absorption is measured. To prevent a high blank, H₃PO₄ is added, forming ferric phosphate complexes which do not absorb appreciably (see Fig. 21.5).

(10) The equation for the oxidation is



PbO₂ or NaBiO₃ also oxidize Mn to permanganate, but are more troublesome to use, since the excess oxidant must be removed by filtration before the absorbance

can be measured. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ with Ag(II) as a catalyst also oxidizes Mn to permanganate, but results seem more erratic than with KIO_4 .

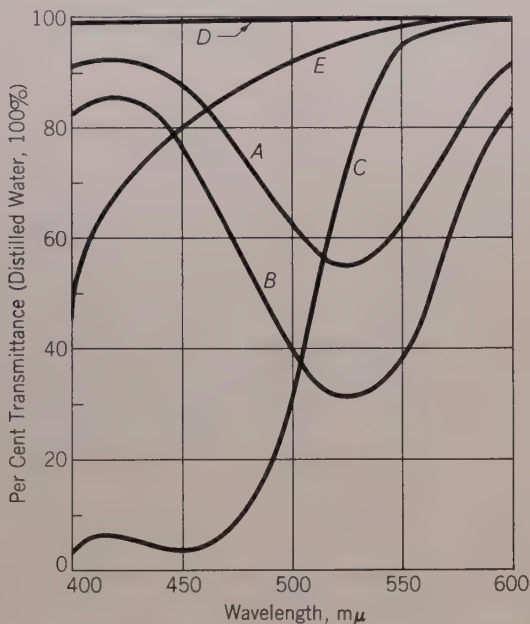


FIG. 21.5. Interferences in the Determination of Manganese in Steels—Curve A: Permanganate, $6\text{ }\mu\text{g}$ Mn per ml. Curve B: Permanganate, $12\text{ }\mu\text{g}$ Mn per ml. Curve C: Dichromate, $200\text{ }\mu\text{g}$ Cr per ml. Compared to the amount of permanganate for curve B, this amount of dichromate is about fortyfold greater than that encountered in a typical carbon steel. Curve D: Fe(III) in $\text{HNO}_3\text{-H}_3\text{PO}_4$ solution, 4.4 mg Fe per ml. 1.1 g of pure Fe were put through the procedure of Exp. 21.1. Curve E: Fe(III) in HNO_3 solution. Composition as for curve D, but without H_3PO_4 . (Reprinted in part from W. Rieman, J. D. Neuss, and B. Naiman, *Quantitative Analysis: A Theoretical Approach*, 3d ed. [New York: McGraw-Hill, 1951], Fig. 54, by permission of the publisher.)

(11) The KIO_4 decomposes slowly in the hot solution, and is therefore added in two batches, to ensure that an excess is maintained. If the second batch does not dissolve completely, the residue may be disregarded, since it will dissolve later upon dilution.

(12) Since errors of several tenths of a per cent are negligible, dilutions need not be critically made, and temperature and calibration corrections need not be applied.

(13) Unless the distilled water is of poor quality and contains reductants, the diluted solution is stable and may be left indefinitely. The excess KIO_4 acts as a "holding oxidant."

(14) Examine the solution for any insoluble residue from the original sample, which might have been transferred into the flask along with the solution. If such a precipitate exists, allow it to settle before withdrawing portions of the solution for absorbance measurements.

(15) The absorption of permanganate is a maximum at $525\text{ m}\mu$, and Beer's law has the best chance of being applicable at this wavelength (see Fig. 21.5).

(16) The percentages of various minor components in a typical manganese steel are as follows:

Element . . .	C	Mn	P	S	Si	Cu	Ni	Cr	V	Mo	Al
Per Cent. . .	0.4	0.8	0.06	0.06	0.3	0.1	0.1	0.3	0.01	0.02	0.04

The percentages of the minor constituents in most carbon and manganese steels do not differ greatly from these values (U4). The colors of Cu, Ni, V, and Mo are not sufficiently intense to interfere, even in amounts a hundredfold greater than for the above typical steel.

Because of the low Cr content of the samples, no provision is made in this experiment for the interference of Cr. Chromium will interfere if present in amounts tenfold greater than the Mn, as in stainless steels (Fig. 21.5).

The interference of Cr may be removed in the following way. The solution whose absorbance is to be measured is divided into two portions. One portion is decolorized by the dropwise addition of KNO_2 solution until the permanganate color just disappears. KNO_2 used in this way does not destroy the color of dichromate or the other metals listed above. The decolorized solution is then used as the reference solution, against which the absorbance of the undecolorized portion is measured; the absorption of colored substances other than permanganate in the sample is thus compensated for. Were a selective reductant like KNO_2 not available, a troublesome separation or a two-color analysis might be necessary.

A critical description of the periodate method for Mn in steels, including ones of high Cr content, has been given (C6). Nordling (N3) recommends EDTA instead of KNO_2 for the selective reduction of permanganate.

(17) Cuvettes are seldom identical, and to prevent error, the same cuvette should be used for the unknown as was used for the standard solutions. Similarly, the same cuvette should be used for the reference solution in all measurements. Other ways of eliminating errors due to nonmatching cells involve calibration. An effective and simple procedure is described by Hamilton (H3).

Always clean the cuvette thoroughly and rinse at least once, or preferably twice, with a portion of the sample before filling. Keep solutions away from the outside of the cuvette and wipe it dry and free of fingerprints before placing it in the cuvette holder. Make sure that no bubbles cling to the inner surface of the cuvette or form there during a reading. Handle and clean the cuvettes carefully to avoid breaking or scratching the optical surfaces. If cuvettes are unmatched, it is desirable to make a reference mark out of the light path on each, and always to place it in the same orientation in the holder.

(18) No blank is determined in this experiment, since there is little likelihood of any appreciable Mn being in the distilled water or reagents.

(19) For minimum reading error, the absorbance should lie between 0.2 and 0.7 (i.e., 20–60% transmittance). If it is much out of this range, a more appropriate sample size should be taken, or a more appropriate dilution should be made.

(20) For excellent work, the range of four absorbance measurements on the same solution should be about 0.005 absorbance unit. If some of the simpler instruments are used without special precautions, a single reading is occasionally subject to fluctuations. Repetition of the measurement guards against large errors due to

such fluctuations. Such repetition is not necessary with high precision instruments.

(21) The two methods of computation are described in Exs. 1 and 2, page 515. The advantages of assuming that Beer's law holds (*Method I*) are speed and simplicity, since only one standard steel sample need be run. The disadvantages are several: A chance gross error in the preparation of the standard steel solution may not be revealed. Also, deviations from Beer's law and errors due to the blank and non-identity of the absorption cells are not exactly compensated for unless the unknown and standard steels have identical Mn contents. If there is a large difference between the unknown and standard steels, it is best to regard the answer obtained from Beer's law as an approximation only. Use of a working curve decreases the chances of error from all these sources, but unless this is done cooperatively by several students, considerable time and effort are required.

(22) For excellent work, the relative standard deviation in Mn content of the points from the smooth working curve should be considerably less than 1%. For highest accuracy, it is recommended that the unknown steel be run in duplicate; in such a case, the relative range in Mn contents of the duplicate samples should be around 1% or less for excellent work.

(23) KMnO_4 may deposit brown films of MnO_2 on the insides of containers. For removal of such films, see Note 3, Exp. 20.2 (p. 486).

QUESTIONS

Section 21A

1. In Fig. 21.1 (p. 506), what scale is proportional to energy?
2. What are the uncertainties of the wavelength and velocity of Prob. 1, Sec. 21A (p. 533)? Speculate on how a length or velocity may be measured with such precision.
3. What is the color of a solution having a strong absorption band from 500–530 $\text{m}\mu$?
4. Assuming that absorption occurs within a single, rather narrow wavelength band, within what wavelength region does a red solution absorb?
5. What is the color of a solution which absorbs strongly in the region from 350–650 $\text{m}\mu$?
6. Describe the color of a substance which absorbs strongly only in the infrared region. Only in the ultraviolet. Throughout the visible region.

Section 21B

1. Why should the absorption spectrum of a substance be known before its spectrophotometric determination is undertaken?
2. Cite the advantages and disadvantages in the use of a wide wavelength interval in a spectrophotometric determination.
3. Give two reasons why a spectrophotometric determination is usually carried out at a wavelength corresponding to a minimum in the transmittance curve of the sought-for substance. Give reasons why a different wavelength might be used in some cases.
4. At what wavelength should the absorbance be measured in order to determine the concentration of a pure but dilute $\text{K}_2\text{Cr}_2\text{O}_7$ solution spectrophotometrically (Fig. 21.5, p. 529)?
5. Draw roughly the absorption curve (i.e., absorbance vs. wavelength) corresponding to curve A, Fig. 21.4 (p. 522).
6. With reference to Fig. 21.5, draw rough absorbance vs. concentration curves for permanganate on a single graph at wavelengths of 525 and 475 $\text{m}\mu$.

7. Explain the nature of the error if an analysis is based on a transmittance (a) far above, and (b) far below, the optimum of 20–60%.

8. A certain colored substance is slowly decolorized by reaction with oxygen in air. If this fact is not known by a worker, what will be the nature of the error caused by this decolorization in the spectrophotometric determination of the substance?

9. Describe specifically the factors that should be controlled in the spectrophotometric determination of Cu as the ammoniacal complex.

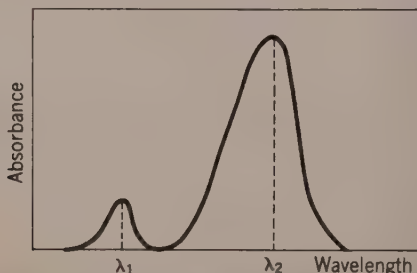
10. Is spectrophotometric determination precluded if a sought-for colorless substance is only partially convertible to a colored complex? Explain.

11. Draw the transmittance curve of a filter that would be suitable for measurement of substance A in the presence of substance B in a filter photometer (Fig. 21.4).

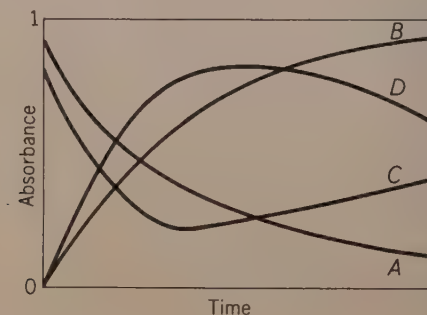
Sections 21C–E

1. Explain how failure to control temperature may cause error in a spectrophotometric determination.

2. For a substance that has the accompanying absorption spectrum, cite conditions under which it might be advantageous to determine the substance at wavelength λ_1 , rather than at wavelength λ_2 .



3. A color is developed for a direct spectrophotometric determination. When the color is unstable, a plot of absorbance vs. time may assume any of the forms shown in the accompanying diagram. Postulate a type of chemical reaction that would explain the change in each case. At what time would it be best to measure the absorbance of a solution behaving as in curve *C*? Curve *D*? In line with the postulations, explain how to change the conditions of measurement so that the methods represented by curves *A* and *B* become more feasible.



4. In the spectrophotometric determination of Cu(II) as the Cu(II)-NH₃ complex, what conditions should be chosen to make the plot of absorbance vs. total Cu(II) concentration as nearly a straight line as possible?

5. Chloride does not absorb in the visible or near ultraviolet regions. However, an indirect method for low concentrations of chloride (10–20 p.p.m.) has been reported, based on the formation of Fe(III)-Cl⁻ complexes that absorb highly at 340 mμ (W10). The color is developed in 5 M HClO₄ with Fe(ClO₄)₃ as a reagent because perchlorate does not complex with Fe(III). In the development of the method, it was found that a plot of absorbance vs. total chloride concentration was not linear except at rather high concentrations of Fe(III). Explain.

6. From information given in the text, give approximately the shapes of the working curves (i.e., absorbance vs. total Cu concentration) for the determination of Cu with dithizone at wavelengths of (a) 510 mμ, (b) 625 mμ.

7. Write equations to show the methylation of a fatty acid by thionyl chloride and methanol in ether solution.

Experiment 21.1

1. Explain the principal function of each of the following reagents, using a chemical equation, if possible. HNO₃, (NH₄)₂S₂O₈, H₃PO₄, KIO₄, oxalic acid (for cleaning).

2. Explain why HCl is not used to dissolve the sample.

3. Suppose that the reagents contain Mn as an impurity, and that the blank is therefore appreciable. Explain how examination of the working curve would reveal such a blank.

4. Outline specifically how to determine the blank, if this is deemed necessary.

5. Suppose a student does not use precisely 0.499–0.501-g samples of unknown and standard steels, but that these lie in the range 0.45–0.55 g. Explain how the method of calculation must be altered from that described in step 5, if (a) Beer's law is used, (b) a working curve is used.

6. When KNO₂ is used to correct for interference due to dichromate (Note 16), explain why an excess of KNO₂ is so carefully avoided.

7. From the data in Fig. 21.5 and the information in Note 16, outline a spectrophotometric method for the determination of dichromate in an acid solution containing K₂Cr₂O₇ and KMnO₄.

8. Speculate as to what might be the nature of the interaction between Fe(III) and permanganate. On the basis of this mechanism, explain how the maintenance of a constant concentration of iron in all unknown and standard solutions compensates for the error.

9. If Fe(III) interacts with permanganate, explain why the use of a comparison solution decolorized by KNO₂ will not compensate for this interaction. For what sort of interference does the decolorization technique compensate?

10. Suppose that a steel contains enough Cr to cause a small but appreciable error in the determination of Mn when the absorbance is measured at 525 mμ. With the aid of Fig. 21.5, explain how this error would be reduced by measurements made at 550 mμ instead of at 525 mμ.

PROBLEMS

Section 21A

1. A sodium vapor lamp emits a very intense radiation with a wavelength of 5889.97 Å. Express the wavelength in centimeters and in millimicrons. What is

the frequency of this radiation? The color? (An accurate value for the velocity of light *in vacuo* is 2.99776×10^{10} cm/sec.)

Ans. 0.0000588997 cm, 588.997 m μ ; 5.08960×10^{14} (sec) $^{-1}$; yellow.

2. In the form of permanganate, 4 μ g of Mn may be easily determined with a standard error of only a per cent or so. What is the molar concentration of Mn(VII) in this solution? Assuming that a spectrophotometric determination is performable with 10 ml of solution, how much Mn is required for a determination?

3. Convert each of the following wavelengths into its corresponding frequency, and calculate the energy per quantum in each case: 450 m μ (blue), 530 m μ (green), 590 m μ (yellow), 700 m μ (red), 2.00 m μ (X ray), 5.00×10^4 m μ (infrared). Explain the significance of expressing the energy per mole of quanta (6.02×10^{23} quanta per mole), and calculate this energy for each of the preceding wavelengths.

Ans. 4.28×10^{14} sec $^{-1}$, 2.83×10^{-12} ergs/quantum,
 1.70×10^{12} ergs/mole (for 700 m μ).

4. X-ray spectrographers prefer to express wavelength in terms of Ångstrom units ($1 \text{ Å} = 10^{-8}$ cm). What are the wavelength (in m μ) and frequency of a 3.00 Å X ray?

Sections 21B-E

1. The intensity of a monochromatic light beam is decreased to 20.0% of the original intensity on passing through 3.00 cm of a 2.00×10^{-4} M solution of an absorbing solute. Calculate the molar absorptivity. *Ans.* 1.16×10^3 .

2. What are the per cent transmittance and absorbance of the light beam after passing through the following solutions of the solute of Prob. 1? (a) 2.00 cm of a 4.00×10^{-4} M solution; (b) 4.00 cm of a 2.00×10^{-4} M solution; (c) 4.00 cm of a 4.00×10^{-4} M solution. *Ans.* (a) 11.8% , 0.928 .

3. Absorbance is plotted against molar concentration for a substance that follows Beer's law. What is the slope of the plot? What datum is needed to calculate the molar absorptivity from the slope? *Ans.* ab ; b .

4. Calculate the transmittances corresponding to the absorbances of Ex. 1, page 515. Plot these transmittances on a log scale against Mn concentrations on a linear scale, using semilog graph paper. Compare the plot with that on page 516.

5. When treated by the procedure of Ex. 1, page 515, a 0.475 -g steel sample gives an absorbance of 0.262 . What is the % Mn in the steel? *Ans.* 0.259% .

6. A 0.300 -g sample of X is dissolved, a colored complex developed, the solution diluted to 500 ml, and the absorbance measured as 0.520 . A 0.700 -g sample containing 0.120% X is treated in the same way, and the resulting solution has an absorbance of 0.600 . Calculate the % X in the sample.

7. A solution containing 3.0 p.p.m. of a colored substance shows a transmittance of 48.3% . What is the concentration of a solution having a transmittance of 28.2% under the same conditions? *Ans.* 5.2 p.p.m.

8. An aliquot of a solution of a colored substance (S) is diluted with an equal volume of distilled water, and the absorbance of the resulting solution is measured as 0.325 . Another aliquot is diluted with an equal volume of a standard solution containing 0.000300 M S, and the absorbance of the resulting solution is 0.657 . Calculate the concentration of S in the original solution. What types of interferences would be compensated for by this procedure that would cause error if the absorbance of the original solution were compared with the absorbance of the standard solution?

9. Using transmittances from curves A and B of Fig. 21.5 (p. 529), calculate two

values for the molar absorptivity of permanganate at 525 $m\mu$. Within the error of reading the plots, is Beer's law obeyed? Assume a path length of 1.00 cm.

Ans. 2.4×10^3 ; 2.3×10^3 ; yes.

10. The element X in a sample is dissolved, a colored complex developed, the solution diluted to 250 ml, and the absorbance measured. One-gram portions of four standard samples and an unknown give the following data:

	SAMPLE NUMBER				
	1	2	3	4	Unknown
Per cent X.....	0.200	0.400	0.600	1.000	?
Absorbance.....	0.190	0.324	0.425	0.602	0.520

- Construct a working curve, and determine the % X in the unknown.
- Using only the data for standard sample No. 4 and the unknown, calculate the % X in the unknown sample, assuming that Beer's law holds.
- Using only the data for standard sample No. 3 and the unknown, calculate the % X in the unknown sample, assuming that Beer's law holds.
- Making use of the working curve, explain the discrepancies among the three estimates of the % X.

11. An important spectrophotometric method for Fe(II) is based on measurement of the intense red-orange color that is formed when *o*-phenanthroline is added to a solution of Fe(II). The system obeys Beer's law in the range 0–8 p.p.m. of Fe(II). A solution containing 0.100 p.p.m. of Fe(II) and excess *o*-phenanthroline gives an absorbance of 0.200 in a 1.00-cm cell. An unknown solution gives an absorbance of 0.470 under the same conditions. (a) Calculate the Fe(II) concentration in the unknown solution in p.p.m. and in moles per liter. (b) Calculate the molar absorptivity of the complex.

Ans. (a) 0.235 p.p.m., $4.21 \times 10^{-4} M$; (b) 1.12×10^5 .

12. A standard solution containing 3 *M* NH_3 and 0.90 mg of Cu(II) per milliliter has transmittance of 26.8% under certain conditions. What is the Cu(II) concentration of an ammoniacal solution that has a 21.5% transmittance under the same conditions?

Experiment 21.1

1. Assuming that the standard steel contains 0.50% Mn, calculate the micrograms per milliliter in the diluted standard steel solution whose absorbance is measured.

Ans. 10.0.

2. What weight of a steel containing 3.5% Mn would have to be taken so that the 250 ml of diluted sample solution would contain 8.0 μg of Mn per milliliter? Explain why such a small sample should not be used. Explain how to modify the procedure of Exp. 21.1 to accommodate samples with such a high Mn content.

3. Show that the absorbance is proportional to the Mn content, if the sample size is constant.

4. How much KIO_4 is theoretically required to oxidize the Mn in a 0.50-g sample that contains 0.50% Mn?

5. Assume for the data of Ex. 1, page 515, that the difference between zero and 0.005 absorbance unit is the smallest that can be detected. Calculate the lowest Mn concentration detectable by this method. To what % Mn would this correspond in a steel sample weighing 0.50 g?

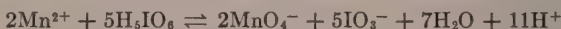
Ans. 0.09 $\mu g/ml$; 0.005%.

6. A 0.500-g sample of a high-manganese steel is treated as in Exp. 21.1, the sample finally being made up to 250 ml of solution. A 0.500-g sample of a standard steel containing 0.320% Mn is treated similarly, and the absorbance of the resulting solution is 0.382. The absorbance of the unknown steel solution is too high to be measured precisely, but a 25.0-ml aliquot diluted with water to 200 ml shows an absorbance of 0.495. Calculate the % Mn in the unknown steel, and explain why the answer is only approximate.

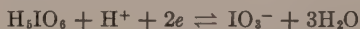
7. Suppose that two cells match when filled with distilled water, but that cell 1 shows 70.0% transmittance, while cell 2 shows 72.0% transmittance for the same solution. What would be the transmittance in cell 1 of a solution that has a transmittance of 23.5% in cell 2? Discuss the error of applying a "common-sense" proportional correction to transmittances measured in cell 2, to make them equivalent to transmittances measured in cell 1. *Ans.* 20.8%.

8. Suppose that two cells match when filled with distilled water, but that cell 1 has an absorbance of 0.200, while cell 2 has an absorbance of 0.210 for the same solution. What would be the absorbance in cell 1 of a solution that has an absorbance of 0.600 in cell 2? Give the correction factor by which absorbances measured in cell 2 should be multiplied to make them equivalent to absorbances measured in cell 1.

9. Periodic acid is a moderately weak acid, having the formula H_5IO_6 , and the equation of Note 10 (p. 528) may more properly be written as



For the conditions of Exp. 21.1, calculate the equilibrium ratio of $[\text{MnO}_4^-]/[\text{Mn}^{2+}]$ in the 250 ml of diluted solution. Make the following simplifying assumptions. (a) Half of the added periodate is reduced to iodate, so that $[\text{IO}_3^-]/[\text{H}_5\text{IO}_6] = 1$. (b) All solutes are completely dissociated, except H_3PO_4 and H_5IO_6 , which are completely undissociated. (c) All activity coefficients are unity. The standard single-electrode potential is 1.60 v for the half-reaction



Discuss the answer.

Ans. 2×10^9 , assuming that $[\text{H}^+] = 0.5 M$.

22 INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

In this chapter, an attempt is made to classify the various methods of measuring the quantity of a substance. Classical and instrumental methods of measurement are defined and contrasted, and the place of instrumentation in analytical chemistry is discussed.

22A. STOICHIOMETRICAL AND NONSTOICHIOMETRICAL METHODS

It is the purpose of a quantitative analysis to determine the weight (or concentration) of a sought-for substance. The most direct way of doing this is to isolate the substance and weigh it. Such a direct procedure is seldom possible, however, because the quantitative isolation of the substance in weighable form is difficult.

In most cases, the amount of the sought-for substance is estimated indirectly. The weight of substance (W) may be deduced from the measured magnitude (X) of some property of the sample that is related to the weight (or concentration) of the sought-for substance. The relationship may be expressed generally as

$$W = f(X, \text{other variables}) \quad (22.1)$$

For the purpose of analysis, so that W may be accurately estimated from X , all variables other than W that affect X must be held constant.

Equation 22.1 is very general, and applies to all methods of determining substances. According to the complexity of Eq. 22.1, analytical methods of measurement may be classified into two groups, stoichiometrical and nonstoichiometrical.

For some methods of measurement Eq. 22.1 has a simple form; W is proportional to X and the proportionality constants may be found from the table of atomic weights and the laws of stoichiometry. Such methods of measurement are best called *stoichiometrical* methods, although the terms "classical" or "chemical" are sometimes used. These methods are emphasized in the elementary course, and they include gravimetric, volumetric, and gasometric analysis. For example, in a gravimetric analysis, W is directly proportional to the weight, X , of isolated precipitate, and the proportionality constant is a gravimetric factor calculable from the table of atomic weights (see Eq. 9.2, p. 143). Similar simple relationships exist for volumetric and gasometric analysis.

Nonstoichiometrical methods are based on properties which cannot be related to W through the laws of stoichiometry. The so-called "physical," "physico-chemical," and "instrumental" methods fall in this class. For many methods, W and X are not at all proportional.

The determination of the H_2SO_4 content of a storage battery by measurement of the density of the solution is an example of a nonstoichiometrical method (Fig. 22.1). The H_2SO_4 content, W , is related to the

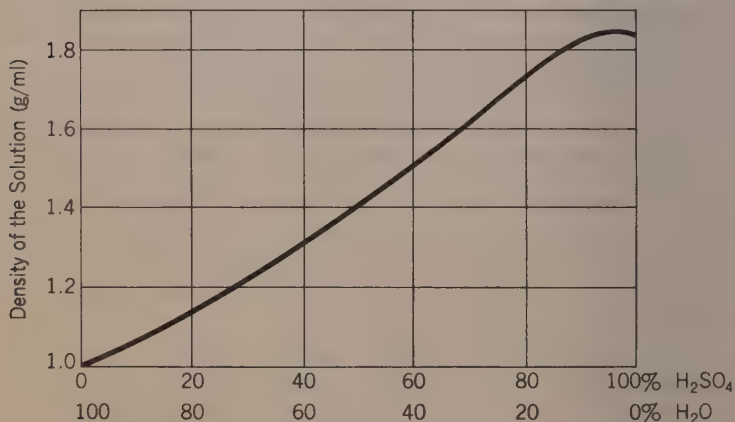


FIG. 22.1. Densities of H_2SO_4 -Water Systems (25°C)

density, X , but not proportionally. Further, the density of a solution with a certain H_2SO_4 content is affected by the temperature and the presence of other solutes, so that the latter two variables must be controlled before the density may be taken as a measure of the H_2SO_4 content.

For nonstoichiometrical methods, Eq. 22.1 is usually too complicated to permit direct calculation of W in terms of X . Nonstoichiometrical

methods are relative and require calibration. Fundamentally, all calibration procedures involve the measurement of X for one or more standard samples of known W , all other variables being kept constant. The calibration empirically defines the relationship between W and X for a fixed set of conditions. After calibration, the measurement of X for an unknown sample permits determination of W . The method of the working curve (Exp. 21.1, p. 526) is one common calibration procedure. Figure 22.1 is a working curve for the analysis of H_2SO_4 solutions by measurement of the density. There are other calibration methods.

The functional simplicity of Eq. 22.1 for stoichiometrical methods is aesthetically satisfying, but the experimental procedure for the measurement of X may be laborious and time consuming. On the other hand, the possible advantages of nonstoichiometrical methods are (1) speed, (2) simplicity, (3) sensitivity, and (4) selectivity. The method of Fig. 22.1 for H_2SO_4 is very simple and rapid. As another example, the spectroscopic method is exceedingly sensitive and selective for many elements.

22B. NONSTOICHIOMETRICAL METHODS

Nonstoichiometrical methods of measurement are classified in the following outline according to the nature of the measurable property. This outline is presented so that the student may obtain an idea of the many methods of measurement that are available to the analyst. Some of these methods are as important as the classical ones, and a few are even more widely used. A description of each of these methods is beyond the scope of this book. Most of the methods are described in elementary texts on instrumental analysis (**D4**, **L14**, **S31**, **W16**), and individual references are given below for methods which do not appear in these elementary texts. Although the treatments in most of these references are simple, principles from several fields of science may be involved. The ease of studying any of these references will therefore depend greatly on the background of the individual student.

- A. Methods depending on measurement of radiant energy
 1. Infrared spectroscopy (absorption)
 2. Visible-light spectroscopy (absorption and emission)
 - (a) Emission spectroscopy (arc, spark, flame)
 - (b) Spectrophotometry and colorimetry (also turbidimetry, nephelometry, and fluorimetry)
 - (c) Raman spectroscopy
 3. Ultraviolet spectroscopy (absorption and emission)
 4. X-ray spectroscopy (absorption and emission)
 5. Neutron spectroscopy (absorption) (**B11**)

6. Methods depending on measurement of radioactivity (α , β , or γ rays)
 - (a) Determination of radio-isotopes by measuring radioactivity
 - (b) Determination of inactive isotopes by induced radioactivity (activation analysis) (C10, K10)
7. Nuclear magnetic resonance spectroscopy (P8)
8. Microwave spectroscopy (absorption) (H12)
9. Refractometry (refractive index)
10. Polarimetry (optical rotation)
- B. Methods depending on measurement of electrical properties
 1. Electrode or membrane potentials
 2. Voltammetry
 - (a) At constant voltage (polarography)
 - (b) At constant current (chronopotentiometry)
 3. Resistance or conductance
 4. Dielectric constant
 5. Magnetic permeability
 6. Mass spectrometry
- C. Methods depending on measurement of thermal properties (not frequently used, but occasionally valuable)
 1. Transition temperature (freezing or boiling point)
 2. Thermal conductivity
 3. Heat of reaction
- D. Methods depending on measurement of mechanical properties (not frequently used, but occasionally valuable) (K18)
 1. Density
 2. Viscosity
 3. Surface tension
 4. Velocity of sound in a gas
- E. Miscellaneous methods
 1. Methods depending on solubility (L16)
 2. Methods involving measurement of reaction rate (catalyzed or uncatalyzed) (K13, M18)
 3. Particle-counting methods
 4. Biological assay (H15, N1)

22C. INSTRUMENTAL AIDS TO TITRATION

22C.1. General Method of Establishing End Points

If in a titrated solution a property is measured that depends upon the concentration of sought-for or standard substance, then this measurement may change throughout the titration, and may change sharply in the region of the equivalence point. To show the change, a titration curve may be plotted, giving the magnitude of the property (ordinates) as a function of the volume of standard titrant added (abscissae). Such titration curves are of two types. (1) Most properties give a broken type of curve (Fig. 22.2), the break in which is taken as the end point. The characteristics of such titration curves are described in greater

detail in the following section. (2) In potentiometric titrations the single-electrode potential follows an S-shaped curve, the point of steepest slope being taken as the end point.

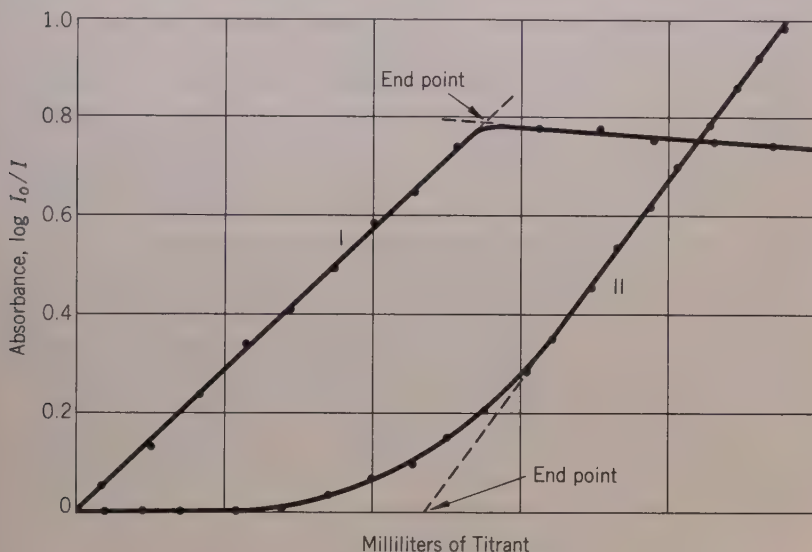


FIG. 22.2. Spectrophotometric Titration Curves

Many of the nonstoichiometrical properties listed in Sec. 22B may be used in the foregoing way to establish the end point in titrations. No matter what property is used to establish the end point, however, the procedures are all titrations, and are not nonstoichiometrical procedures. Even though an instrument is used to establish the end point, the amount of sought-for substance is still calculated stoichiometrically from the volume of standard titrant used, and not from any measured value of the indicator property.

22C.2. Spectrophotometric Titrations (H6, U2)

Suppose that a titration is based upon the reaction



If a reagent or product absorbs light, such absorption may be used to establish the end point. For example, if AB is colored (A and B being colorless), the absorbance of the solution increases as titrant is added up to the equivalence point; beyond the equivalence point, the absorbance decreases slightly, owing to dilution. For this particular case

a broken titration curve similar to curve I in Fig. 22.2 is obtained. If the titrant B is colored (A and AB being colorless), the titration curve remains horizontal at zero absorbance up to the equivalence point; beyond the equivalence point, the absorbance increases as B is added (curve II, Fig. 22.2). In general, the titration curve may have either increasing or decreasing fore- and afterslopes, depending on which ones of the substances (A, B, or AB) are colored.

With this technique, milligram quantities of Cu and Ni are titratable at the 0.1% error level with a standard solution of the disodium salt of ethylenediaminetetraacetic acid (EDTA). Even in dilute solutions Cu(II) and Ni(II) form very tight complexes with EDTA, these complexes being more intensely colored than the hydrated ions.

To obtain the titration curve, standard solution is added in finite increments, and the absorbance is measured and plotted after each increment.* This is done for several points before and after the end point, which is then located as the intersection of the two curve segments drawn through the two groups of points before and after the end point. This mode of selecting the end point is indicated in Fig. 22.2. Grunwald has given a general method for selecting the end point on a broken type of titration curve (G6).

A titration curve of the broken type should have three desirable characteristics. (1) The break should be sharp—that is, the volume range over which the slope transits from the fore- to the aftervalue should be small. (2) The magnitude of the break should be great—that is, there should be a great difference between the fore- and afterslopes. (3) There should be little curvature in the fore- and aftersegments, so that extrapolation of the segments may be easily made to find the intersection. Although a complete discussion of the factors which affect the shape of the curve and the sharpness of the break cannot be given here, a listing of these factors indicates the limitations of the method, and shows what variables must be controlled for good results.

The sharpness of the break is determined by the completeness of the titration reaction. If AB is highly undissociated or very insoluble, the break is sharp (curve I, Fig. 22.2). If AB is appreciably dissociated or soluble, the titration curve is rounded in the region of the end point (curve II, Fig. 22.2). In the latter case, extrapolation of the fore- and aftersegments may still be made to establish the end point, although the chances of error increase as the curvature increases. Such extrapolation may be made with passable accuracy (i.e., errors of the order of 1%) even for reactions so incomplete that the use of a chemical indi-

*If a recording spectrophotometer is used, the manual effort of reading and plotting absorbance is eliminated (M5).

eator would be out of the question. This is a particular advantage of the broken type of titration curve.

The magnitude of the break and the straightness of the fore- and aftersegments are determined by many factors which do not affect the sharpness of the break. Some of these factors are (1) an increase in volume of the system as titration progresses; (2) relative concentrations of the titrated and standard solutions; (3) the presence of other colored substances. These factors should be carefully controlled, for the detectability of a break may be augmented by their proper regulation or may be greatly reduced by their neglect. This statement applies generally to other types of titrations that give broken titration curves; in each case a number of factors must usually be controlled to give a good end point.

Even for cases where A, B, and AB are all colorless, the spectrophotometric technique may be used with an indicator. An indicator substance is one that undergoes a color change on reaction with excess A or B. In order that a sharp end point may be obtained, it is necessary that the indicator react with A or B quite completely, but not nearly so completely as A and B react with each other. In this way, milligram quantities of Fe(III) are titratable in dilute solutions with standard EDTA, an excess of salicylic acid being used as an indicator to form a highly colored complex with Fe(III) (S33).

22C.3. Titrations Based on Measurement of Other Properties

Instead of transmittance, other properties of the titrated system may be used to establish the equivalence point. Among such properties are:* (1) light emission in a flame, measured with a flame photometer; (2) turbidity produced as a result of the titration reaction, as in heterometric titrations (B17); (3) radioactivity, a radiotracer being added to the titrant or sought-for substance (L5); (4) single-electrode potential, as in a potentiometric titration (p. 445); (5) electrolysis current, due to oxidation or reduction of a reagent or product at an electrode, as in an amperometric titration; (6) time required for discharge of a reagent or product species at constant current, as in coulometric or chronopotentiometric (R7) titrations; (7) conductance (p. 289); (8) heat of reaction (L10); (9) volume or pressure, for titrations in which a gas is formed (G5), or for gas titrations (K2).

The broken type of curve is obtained for all of these methods except the potentiometric, which gives an S-shaped curve. Most of these methods are restricted in their application, even though each may be useful in special cases.

*Literature references are given only for those methods that are not described in elementary instrumental analysis texts.

22C.4. Instrumental Titration Methods Compared with Other Methods

22C.4a. Chemical indicators versus instruments for the establishment of end points. If sufficiently accurate, a chemical indicator is generally preferred to an instrumental method, since the time, effort, and expense involved are usually less. However, there are several important situations for which instrumental methods are best. (1) Some reactions adequately fulfill the requirements for good titration procedures, but no chemical indicators are available. (2) Sometimes the color change of a chemical indicator may be obscured by other colored or suspended materials in the solution. (3) For nonroutine use in investigating the accuracy of a method, or where high accuracy is desired, an instrumental method may eliminate all error associated with a chemical indicator. (4) The use of instruments may allow a routine titration procedure to be put on an automatic basis, saving manpower.

22C.4b. Advantages of instrumental titration methods. The magnitude of the property employed to establish an end point could itself be taken directly as a measure of the amount of the sought-for substance. As an illustration, the titration of Cu described on page 542 could be done spectrophotometrically after addition of excess $\text{Na}_2\text{H}_2\text{Y}$, simply by taking the transmittance of the solution as a measure of the amount of Cu.

It is generally true that the determination by measurement of a property is more rapid and direct than is the use of that property in establishing an end point in a titration. However, the instrumental titration procedure has advantages: (1) The titration is stoichiometrical. (2) When the magnitude of a property is used directly to determine the amount of a substance, the accuracy depends on how accurately the property is measured. On the other hand, if the property is used to establish an end point, only gross changes or discontinuities in the magnitude of the property are sought as titrant is added; therefore, the property need not be so accurately measured, and conditions need not be so stringently controlled. The accuracy of the titration generally depends not on how accurately the property is measured, but rather on how accurately the volume and concentration of the standard solution are known. The titration procedure is therefore generally more accurate.

22D. INSTRUMENTATION IN ANALYTICAL CHEMISTRY

22D.1. Control and Automation

In chemical industry, the usual purpose of a chemical analysis is to find out something about a product (i.e., whether or not it is up to specifications) or a process (i.e., whether or not it is operating properly).

In such cases the result of the chemical analysis is interpreted as a basis for action by the plant workers, and the product is passed or rejected, or some adjustment is or is not made in the process. This general procedure of analyzing, interpreting, and taking action is called "controlling" the product or process. This is why routine analytical work in industry is often called *control work*.

Figure 22.3 illustrates the control operation as a *feedback loop*, which begins with an analysis of some part or parts of the process (including its raw materials or products), and which results in some action on the process (including its raw materials or products). The purpose of the loop is to regulate the process so that it meets certain specifications as determined by the analysis. The feedback loop itself may range from very simple to very complex. It may consist of one or many operations. It may involve much manpower or be automatic. The feedback loop may have several points of origin and several points of termination—i.e., the loop may consist of a number of component loops.

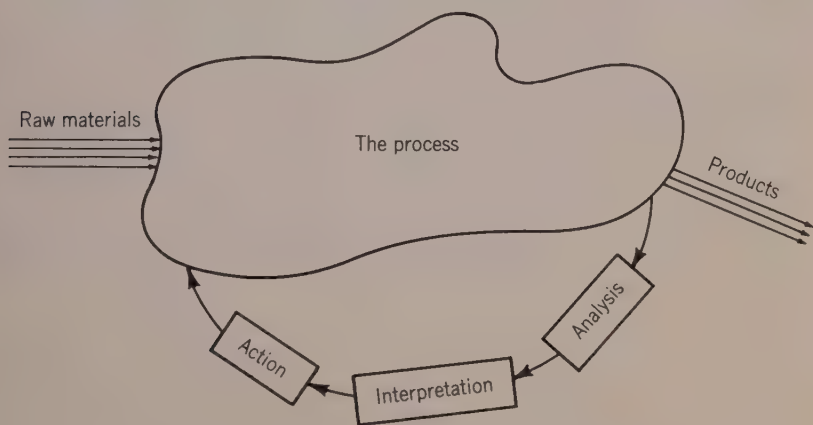


FIG. 22.3. The Control Operation as a Feedback Loop

In industry there is a constant striving to make the control operation automatic, in order to reduce the human effort required. The science or technology of making processes automatic is called *automation*. So long as classical methods of analysis are used, there must be much human effort involved, not only in analyzing but also in interpreting and taking action. If instrumental methods of analysis are used, control is much more amenable to automation; the result of an instrumental method of analysis is usually an electrical or mechanical impulse which, if properly utilized and fed back into the process, may make control

completely automatic, without the necessity for interpretation or action by man.

A simple example may illustrate the difference between nonautomatic and automatic control. Suppose that an industrial reaction occurs in a large tank, complete with stirrers, etc. All raw materials except H_2SO_4 are charged batchwise into the tank. However, the reaction is slow and consumes H_2SO_4 , which must be added slowly to keep the pH between 3.7 and 4.6 (critical allowable limits). The reaction is judged to be complete when the rise from pH 4.0 to 4.3 requires longer than a certain, specified length of time—after the H_2SO_4 stream is off, of course. At this point, the tank contents are stirred until the pH rises to 4.6; then the contents are transferred by pipeline to the next stage in the process, the tank is recharged, and the cycle is repeated.

Nonautomatically, this operation might be controlled as follows: (1) Samples are withdrawn periodically, taken to the control laboratory, and the pH of each sample determined. (2) As each pH result is reported, it is examined, a decision is made, and a command is forwarded to the operator of the H_2SO_4 valve. These commands, dependent upon the pH value, are: pH 3.8–4.0, stop H_2SO_4 ; pH 4.0–4.3, no action; pH 4.3–4.5, add H_2SO_4 . These three commands are for normal operation. For safety, to provide against accidents, and to prevent loss of the batch, there must be two more commands, with the realization (and hope!) that they may never be used: pH 3.75–3.80 or 4.50–4.55, alarm and investigation; pH less than 3.75 or greater than 4.55, emergency action to save the batch. (3) The H_2SO_4 -valve operator carries out the commands. To perform these functions, one or more persons must be on the job at all times, and considerable manual effort is required.

Contrast this mode of operation with the automated way. First, the pH electrodes are placed directly in the tank, and the pH meter arranged to record pH continuously, a recording meter being used instead of the usual dial meter in the pH instrument. Next, the electrical output of the pH meter is amplified and fed back by a discriminating unit to a solenoid (magnetic) valve governing the flow of H_2SO_4 so that (1) the valve is closed if the pH is below 4.0; (2) there is no action if the pH is between 4.0 and 4.3; (3) the valve is open if the pH is above 4.3; (4) there is an alarm if the pH reads below 3.8 or above 4.5. All routine human effort is eliminated. There is required only a man in partial attendance to provide emergency action, which will rarely arise in a well-designed process. The preceding automation does not extend to charging and discharging the tank, but these steps might also be made automatic without difficulty, as might even the rare operations of answering the alarm and saving the batch.

Several industries are highly automatic; perhaps the outstanding chemical example is the petroleum industry.

Automation in American industry is increasing phenomenally. It is the consensus that the potentialities of automation have just begun to be realized, and that the point of diminishing returns has by no means been reached, in spite of expense and complexity. Therefore a knowledge of instrumental methods and of the principles of control and automation is today a necessity in the training of every analyst.

22D.2. Automation and the Analytical Process

When analytical procedures are used in automated processes, then of course the analytical process itself should be automated. Much current research is concerned with automating the analytical process in all of its parts: sampling, sample preparation, separations, measurement, and computation.

Preferably, an automated method of analysis should give a rapid, direct, and continuous analytical record. The attempt to achieve these

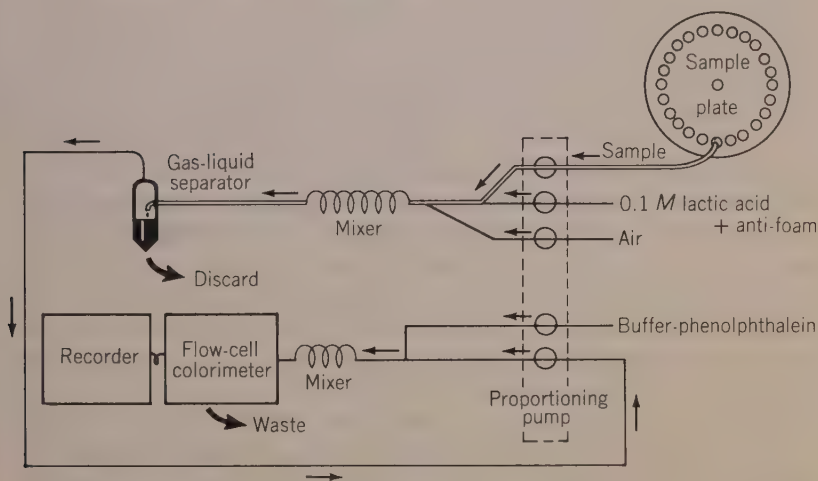


FIG. 22.4. Automated CO_2 Determination (Reprinted from L. T. Skeggs, *Annals of the New York Academy of Sciences*, 87, 651 [1960], Fig. 1, with permission of the New York Academy of Sciences.)

characteristics in an automated procedure usually causes it to lose all resemblance to a manual method for the same kind of analysis.

An example of an automated procedure for the determination of CO_2 in blood serum is given schematically in Fig. 22.4 (S16). In outline, the

procedure is designed to remove the CO_2 from interferences in a small (0.2 ml) serum sample, and then to determine it spectrophotometrically. In detail, the CO_2 is removed by pumping the sample stream into an acid reagent stream and an air stream, all at constant rates through a small proportioning pump. The partial pressure of CO_2 that is established in the gas phase is proportional to its concentration in the sample. The gas stream is then separated from the liquid phase and pumped steadily into an alkaline carbonate-bicarbonate buffer stream containing phenolphthalein. The alkaline solution absorbs the CO_2 , which decolorizes the indicator. The greater the CO_2 content, the greater the decolorization. The phenolphthalein solution is pumped steadily through the cell of a filter photometer, where the absorbance is measured and recorded continuously. The recorder deflection is quite proportional to the CO_2 content of the sample. Calibration is performed by running a standard Na_2CO_3 solution.

While the procedure is particularly amenable to measurement of a flowing sample stream, there is great value in clinical work to the analysis of a series of samples. These are held in a plate that rotates periodically, introducing each sample to the intake tube for a fixed length of time, sufficient for the response to be recorded. Samples can be analyzed at the rate of 40 per hour.

Because of the benefits of instrumentation, it is easy to acquire the idea that instrumentation and automation are the expanding fields of the future, and then to reason (incorrectly) that classical methods of analysis will soon be obsolete. Nothing could be farther from the truth. Instrumental and classical methods are not opposed—they supplement each other. Although instrumental methods are exceedingly useful and necessary, they are not the panacea that will eliminate the slower and more laborious chemical methods. Instrumental procedure should be regarded in its proper perspective—as a very helpful and necessary *part* of the analytical process, in which the classical techniques and methods also have their unique and proper places.

Furthermore, the function of the analytical chemist will not be superseded by the automatic process. The wide use of automation and instruments will probably be limited by two factors for a long time to come. (1) An automatic process is very expensive, and requires much equipment and maintenance. Automation is pointless and uneconomical unless there is assurance that the process will be used sufficiently to recover the expense. (2) Until thinking machines are available with much more variability than the ones we can now design, automatic control will be limited only to repetitive, routine processes. Automatic control does not substitute for or replace the functions of the analytical chemist—it can only supplement and extend his techniques. Automa-

tion reduces the humdrum, routine part of the analyst's work. But the analytical chemist will still be required to design and perform all the parts of an analytical process which are not routine, and which are of an occasional, research, or creative nature; for these functions, there can be no automation.

22D.3. Instrumentation in Elementary Quantitative Analysis

In order to be understood and used properly in analysis, an instrumental method should be studied as follows: (1) The theory and methods of measuring the property X (Eq. 22.1, p. 537) should be studied and learned. This study usually extends to fields other than chemistry. In spectrophotometry, for example, the measurement of light absorption relates to optics and electricity. (2) Next, the relation between X and W must be learned. This is not difficult. Sometimes there is a simple, ideal relationship between X and W , but more often an empirical relationship is used in practical analysis. (3) Also, the dependence of X upon factors other than W should be learned, since these factors must be held constant during analysis if X is to be a valid measure of W . For any one instrumental method there are usually many such factors, each one requiring rather detailed study. Most sources of error and limitations of the method depend upon these factors. For example, a list of variables that affect transmittance in spectrophotometric methods is given on page 513. (4) Finally, the general applications of the method should be learned, together with a few specific examples.

Phases 2 and 4 are not hard to study superficially at the sophomore level, but phases 1 and 3 require a background which the student does not possess until he is a senior or a graduate student.

Phase 1 may be circumvented by regarding the instrument as a "black box" (contents unknown) which measures W in terms of X , and by learning how to turn the knobs on the box in order to make this measurement. A little of this is fine, because it acquaints the student early with instruments that he must eventually use. However, analytical methods learned in this way become rituals, rather than logical procedures. Too much of this sort of thing develops a technician who is little more than an unreasoning extension of the instrument that he manipulates.

In spite of their importance, it appears, therefore, that instrumental methods cannot be studied efficiently in the elementary analytical course, and must be deferred. In this book the object is simply to point out the existence of such methods to the student, and also, by way of illustration, to give some details on electrochemical methods and spectrophotometry. More than this must await an advanced course of instruction.

EXPERIMENT 22.1. POTENTIOMETRIC DETERMINATION OF CHLORIDE

INTRODUCTION

In this experiment, the chloride concentration in a sample solution is determined nonstoichiometrically by measuring its single-electrode potential with an Ag-AgCl electrode. The theoretical groundwork is laid in Chapters 19 and 20, on redox equilibria and titrations. The method is simple; only a potentiometer and a pair of Ag-AgCl electrodes are required. The method is also sensitive and accurate, errors being below 1% with simple precautions.

THEORY

In general, the voltage of an electrochemical cell depends on its composition. Analytical use may be made of this fact; if a sample solution is made a part of an electrochemical cell, measurement of the cell voltage permits calculation of the composition. Suppose, for instance, that a sample solution whose chloride concentration is to be determined is made a part of the following cell.



The cell voltage (V) is a function of many variables, including the sought-for chloride molarity, X .

$$V = E_s + E_{j, s-b} + E_{j, b-u} - E_u$$

E_s and E_u are the single-electrode potentials of the standard and unknown solutions. $E_{j, s-b}$ is the junction potential in passing from the standard to the bridge solution, while $E_{j, b-u}$ is the junction potential in passing from the bridge to the unknown solution. The junction potentials depend in a complicated and undefined way upon the compositions of the solutions (p. 446). However, with the Nernst equation, E_s and E_u may be expressed in terms of the chloride molarity and the activity coefficient in each solution.

$$\begin{aligned} V &= E^\circ_{\text{Ag, AgCl}} + 0.0591 \log A\gamma_{\text{Cl}, s} + E_{j, s-b} + E_{j, b-u} \\ &\quad - (E^\circ_{\text{Ag, AgCl}} + 0.0591 \log X\gamma_{\text{Cl}, u}) \\ V &= 0.0591 \log \frac{A\gamma_{\text{Cl}, s}}{X\gamma_{\text{Cl}, u}} + (E_{j, s-b} + E_{j, b-u}) \end{aligned}$$

If the compositions of the unknown and standard solutions were completely unrelated, V would depend upon too many variables to permit

being taken as an accurate measure of the sought-for chloride concentration, X . However, a way exists out of this difficulty because the compositions of the solutions can generally be adjusted before measurement. Suppose, for example, that the sample solution is a natural hard water that might typically contain 10 p.p.m. of chloride ($3 \times 10^{-4} M$), along with comparably low concentrations of many other kinds of ions, such as Na, Ca, and Mg. In this case, an aliquot of sample may be mixed with a large amount of an inert electrolyte, like H_2SO_4 , to bring the resulting solution to so high a concentration of H_2SO_4 that all other ions that may be in the sample do not contribute significantly to the ionic strength. The standard solution may be brought to the same H_2SO_4 concentration, so that the ionic strengths of the sample and standard solutions are practically identical. Then, $\gamma_{Cl, s} = \gamma_{Cl, u}$, and also, the junction potentials cancel, being equal but opposite in sign. Then, V becomes a simple function of the sought-for concentration, X .

$$V = 0.0591 \log (A/X) \quad (22.4)$$

$$X = A/10^{V/0.0591} \quad (22.5)^*$$

Equation 22.5 is the basis of a method for determining low chloride concentrations (10^{-3} – $10^{-6} M$) that has been used for several decades on diverse samples ranging from natural waters to biological fluids (B14, S28). There are commercial instruments that are based on this method.

PROCEDURE

In this experiment, samples containing 0.0004–0.001 M chloride are determined.

A measured volume of a master sample solution (Note 1) is issued to the student, who adds a fixed amount of H_2SO_4 and dilutes to volume. A standard solution is prepared in similar fashion. The voltage of the unknown solution is measured against the standard, using a potentiometer. Equation 22.5 permits calculation of the chloride concentration in the diluted sample solution, which in turn permits calculation of the chloride content of the issued sample.

1. *Withdrawal of the sample.* Each student is scheduled in advance to use the potentiometer, and he must plan to carry out the measurements within his allotted time. A 250-ml volumetric flask should be

*There is a matter of sign in Eq. 22.5 that requires care to prevent confusion. It is best to consider only absolute values of V , and to calculate the factor $10^{V/0.0591}$, which is always unity or greater. The polarity of the sample electrode will tell whether X is greater (sample electrode is negative) or less (sample electrode is positive) than A . In the case that X is greater than A , A is multiplied by $10^{V/0.0591}$ to give X ; while if X is less than A , A is divided by $10^{V/0.0591}$ to give X .

labeled with the student's name, locker number, and experiment number, and deposited with the instructor during the laboratory period preceding the one scheduled for use of the potentiometer. The sample may then be drawn by the student at the beginning of the scheduled period.

2. *Dilution of the sample.* Prepare about 100 ml of 1.0 M H_2SO_4 (Note 2). Add a 25-ml aliquot (Note 3) of the 1.0 M H_2SO_4 to the sample flask, and dilute to volume with distilled water.

3. *Preparation of the standard solution.*

3a. Dry a 0.5-g portion of reagent-grade NaCl in a weighing bottle at 105°C for an hour. Let the closed bottle cool in air for $\frac{1}{2}$ –1 hour, and then weigh out a 0.292–0.293-g portion (Note 4) into a small beaker. Transfer to a 100-ml volumetric flask and make up to volume to give a 0.0500 M NaCl solution.

3b. Put a 5-ml aliquot (Note 3) of the 0.0500 M NaCl into a 250-ml volumetric flask, add a 25-ml aliquot (Note 3) of the 1.0 M H_2SO_4 , and dilute to volume with distilled water. The chloride concentration in the diluted solution is 0.00100 M .

4. *Potentiometric measurements.*

4a. *Equipment. Rinsing of electrodes.* Figure 22.5 is a schematic of the electrode-bridge assembly. Construction of the components is described in the Supplement (p. 895). In stand-by condition, the electrodes are immersed in 100-ml beakers containing 0.1 M H_2SO_4 . To make a measurement, fill a 50-ml beaker with standard solution, and another with the sample solution. Both beakers should be labeled (Note 5). Place the two beakers on the ringstand adjacent to each other and directly in front of the stand-by beakers. Raise the electrode-bridge assembly until it clears the stand-by beakers (Note 6). Open the screw clamp momentarily, until air is drawn into the bridge arms (Note 7). While the assembly is still poised over the stand-by beakers, rinse the electrodes and bridge ends by pouring over each a little of the solution into which each is to be immersed. Let the rinsings fall into the stand-by beakers. Soak off any large drops adhering to the ends of the bridge and electrodes by touching them lightly with a paper tissue.

4b. *First voltage measurement.* Slide the electrode-bridge assembly forward and immerse the electrodes into the sample and standard solutions. Refill the bridge by opening the screw clamp just long enough to displace all air in the bridge. Equalize the solution levels in the beakers by adding sample and standard solutions, if necessary (Note 8). Read the cell voltage, V_1 (Notes 9, 10).

4c. *Second voltage measurement.* (Note 11.) Raise the electrode assembly, and slide it back so that it is poised above the stand-by beakers. Interchange the standard and sample solution beakers. Repeat the draining of the bridge and the rinsing of the electrode and

bridge ends as described in step 4a. Then measure the cell voltage (V_2) as described in step 4b. After the voltage readings have been made, measure the temperature of each solution before discarding it. (Notes 12, 13.)

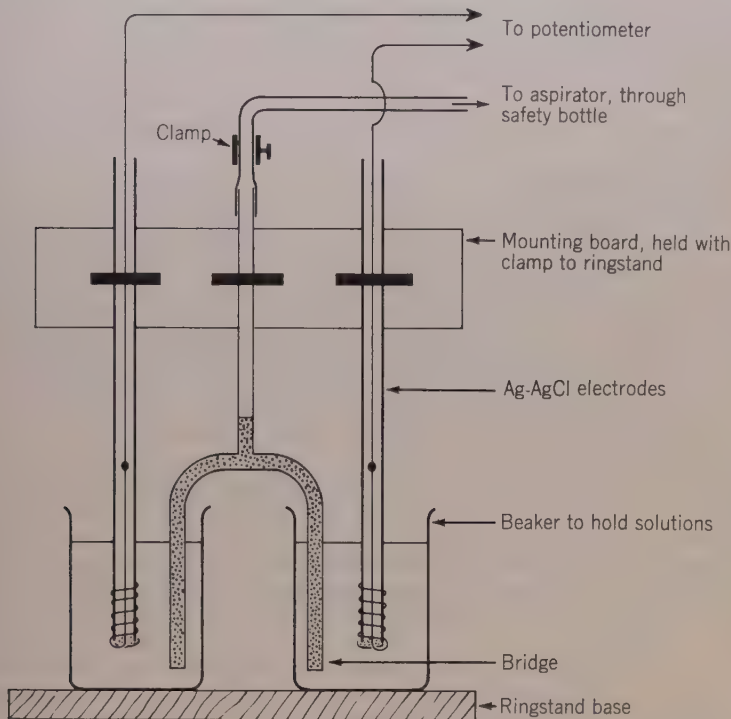


FIG. 22.5. Equipment for the Potentiometric Determination of Chloride

4d. Check to guard against contamination. To reveal other sources of error, it is desirable to repeat the pair of voltage measurements on fresh portions of the sample and standard solutions, especially if the difference between V_1 and V_2 exceeds a millivolt or so.

4e. *Stand-by.* Dilute the remaining 1 M H_2SO_4 tenfold. Rinse the stand-by beakers with a few portions of the diluted H_2SO_4 , and then fill them. Immerse the electrodes in the stand-by beakers. Open the screw clamp for a few seconds to flush the bridge. Short the electrodes with a copper wire. (Note 14.)

5. *Calculations.* From the best value of the cell voltage, and from the known concentration of the diluted standard solution, calculate the chloride molarity in the diluted sample solution. Then calculate and report the chloride content of the sample, as mg NaCl.

NOTES

(1) A master sample solution that contains 0.0100 M NaCl may be prepared by the instructor, by dissolving 5.84–5.85 g of dried reagent-grade NaCl in 10.0 l of distilled water. Issuance of 10–25-ml aliquots will give chloride concentrations in the diluted solutions ranging from 0.0004 to 0.001 M , which is a good range for measurement. For concentrations much above 0.001 M , the sample contributes appreciably to the ionic strength of the diluted solution, and departures from Eq. 22.5 occur. For concentrations much below 10^{-4} M , the chloride blank and the solubility of AgCl contribute significantly to the chloride concentration in the diluted solution, and Eq. 22.5 assumes a more complicated form, as described in the Supplement (p. 897).

(2) The H_2SO_4 need be only approximately 1 M , provided that the same batch of 1 M H_2SO_4 is used to prepare both the sample and standard solutions. It is only necessary that the H_2SO_4 concentration be the same in both diluted solutions.

(3) The aliquot should be measured accurately with a volumetric pipet.

(4) The amount of NaCl is chosen so that the concentration of the diluted standard solution will be 0.00100 M . This is not necessary; any concentration around 0.001 M is suitable, providing that it is known within an error of one per cent.

(5) There will be much manipulation of the sample and standard solutions in the following measurements. Take care to prevent mix-ups.

(6) Be careful not to bump the electrodes against the beaker walls, lest some of the AgCl coating be chipped off.

(7) The solution is withdrawn from the bridge so that no siphoning or displacement of the bridge contents will occur into the standard or sample solutions when the assembly is immersed.

(8) After the electrodes are immersed, the bridge should be filled and the solution levels equalized without undue delay. If left for a long time, contamination or dilution of the sample or standard solutions by the original bridge solution may occur.

(9) Obtain explicit directions on the use of the potentiometer from the instructor.

(10) A few minutes may be required for voltage equilibrium. Make voltage readings at half-minute intervals, rotating the beakers gently between readings to stir the solutions around the electrodes.

(11) Two electrodes of the same kind often exhibit small voltage differences (i.e., *asymmetry potentials*) when immersed in the same solution. If the measured voltage includes such an asymmetry potential, it will cause error if used in Eq. 22.5 to calculate the concentration of the sample solution. To evaluate and correct for such an error, a second voltage reading (V_2) is made after interchanging the sample and standard solutions, so that the electrode that was immersed in the sample solution for the first voltage reading is immersed in the standard solution for the second voltage reading. The cell voltage, corrected for the asymmetry potential, is taken as the average of V_1 and V_2 .

(12) The Nernst constant (0.0591) is temperature dependent, increasing with temperature (p. 406). For very precise measurements, use of the value 0.0591 would require that the solutions be thermostatted at 25°C. However, thermostating is somewhat troublesome. Instead, a simpler procedure is to measure the average temperature of the solutions after the voltage readings have been made, and then to apply a temperature correction of 0.34% per °C to the term (B5). Thus, at 20°C, the Nernst constant is 5×0.34 , or 1.7% less than at 25°C, giving a value of 0.0581.

(13) High accuracy in the measurement of V is not necessary in this determination. The concentrations of the standard and sample solutions are of the same order of magnitude, and V is small (typically 20 mv). Therefore a sizable relative error in V is permissible for a given absolute error (say 0.1 mv). This experiment points up the advantage of making measurements *differentially*. (See Prob. 4, p. 557.)

(14) If there is any asymmetry potential, it will be diminished by immersing the electrodes in the same solution and shorting them.

QUESTIONS

Sections 22A, B

1. Show that Eq. 9.2 (p. 143) and the equation in Prob. 19a (p. 244) are simple forms of Eq. 22.1 (p. 537).

2. Are all nonstoichiometrical methods classifiable as "instrumental" ones? Are all instrumental methods nonstoichiometrical ones? (The answers to these questions may indicate the looseness of the term "instrumental methods.")

3. State the composition region in which the measurement of density would not give a good estimate of the composition of H_2SO_4 -water systems (Fig. 22.1, p. 538). For a sample in this region, devise a procedure whereby a single density measurement would permit an accurate estimate of the composition.

4. Prepare a 5-minute oral report of the methodology, applications, and limitations of one of the nonstoichiometrical methods listed in the outline on page 539.

5. In what class of methods should a blood count be placed?

6. *Lebistes reticulatus* (i.e., guppies) are very sensitive to traces of metal ions. Typically, $4 \times 10^{-8} M \text{Ag}^+$ causes the deaths of half of the guppies in a community within 24 hours. Analytical use may be made of this fact (S12). If a sample containing Ag^+ is added to a 2-l beaker containing about 50 guppies, the percentage of guppies that die within 24 hours increases with the Ag content of the sample. Deduce the shape of the working curve (percentage of dead guppies vs. Ag^+ concentration).

Section 22C

1. A spectrophotometric titration is based on the following reaction:



X is colorless. At the wavelength chosen, both Y and XY absorb, but XY absorbs less strongly than Y. Sketch the spectrophotometric titration curve.

2. Outline how the end point might be established spectrophotometrically in the titration of an FeSO_4 solution with standard $0.1000 M \text{K}_2\text{Cr}_2\text{O}_7$. Consider carefully the absorption of the reagent and product ions, and sketch a typical titration curve. Specify a wavelength for the titration.

3. Sketch approximate curves for the following titrations. (a) Spectrophotometric titration of a dilute CuCl_2 solution with standard EDTA. (b) Spectrophotometric titration of a dilute FeCl_3 solution, containing an excess of salicylic acid as an indicator, with standard EDTA. (c) Conductance against volume of standard base, when $0.1 M \text{HCl}$ is titrated with standard $0.1 M \text{NaOH}$. (Note: H_3O^+ and OH^- are more mobile and conduct more efficiently than other ions, such as Na^+ and Cl^- .) (d) Conductance against volume of standard solution, when $0.1 M \text{AgNO}_3$ is titrated with standard $0.1 M \text{NaCl}$. (e) Temperature against volume of standard solution when $1 M \text{HCl}$ is titrated with standard $1 M \text{NaOH}$, both solutions being initially

at room temperature. (Assume no heat leakage from the titration system.) (f) Pressure against volume of anhydrous NH_3 , when HCl in dry air is titrated with gaseous NH_3 . The HCl sample is in a closed container of fixed volume, with a pressure gauge. The NH_3 gas is forced into the container from a gas buret.

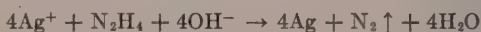
4. Water in fuming HNO_3 may be determined by conductometric titration (H11). The sample is dissolved in anhydrous acetic acid and titrated with a standard solution of acetic anhydride in acetic acid. Sketch the titration curve.

5. A precipitation titration may be followed by measuring the turbidity throughout the titration. Sketch a curve for the titration of AgNO_3 with standard NaCl .

6. A sample of NaCl may be titrated with standard AgNO_3 containing a minute amount of radioactive AgNO_3 . Outline how this titration might be performed, and sketch a titration curve.

7. Outline how the titration of NaOH with standard HCl might be performed by following the heat of reaction.

8. AgNO_3 may be titrated gasometrically with standard hydrazine (N_2H_4), according to the following equation. Sketch a typical titration curve (i.e., milliliters of gas liberated vs. milliliters of standard N_2H_4).



9. Report on methods of titration in which the end point is established by taste or odor (P4).

Section 22D

1. Design an automatic spectrophotometric method of determining Fe(III) at 0–2 p.p.m. in a feed stream to a chemical plant. The method should provide for occasional standardization, should give a continuous record of the Fe(III) concentration, and should give an alarm if the concentration exceeds 1.5 p.p.m.

2. Explain how the sensitivity of the automated procedure for CO_2 (p. 547) is related to the buffer capacity and flow rate of the buffer-phenolphthalein reagent.

Experiment 22.1

1. Explain the advantages of using an acid like H_2SO_4 as the inert electrolyte, rather than a salt like Na_2SO_4 .

2. Explain what dissimilarities between two Ag-AgCl electrodes might cause an asymmetry potential.

3. Explain how the presence of a chloride complexer like Fe(III) might cause error in the determination. How might Exp. 22.1 be modified to accommodate low concentrations of Fe(III) (i.e., 0.001 M) in the sample?

4. According to Eq. 22.4, a plot of $\log X$ (ordinates) against V (abscissae) is a straight line. In reality, however, this equation holds only for values of X above $10^{-4} M$. Show what happens to the plot as X approaches the solubility of AgCl (about $10^{-6} M$), and as X approaches zero.

5. Describe the reasoning that leads to the statement on page 551, that X is less than A if the sample electrode is positive with respect to the standard electrode.

PROBLEMS

Section 22C

1. An $\text{HCl-H}_3\text{PO}_4$ solution containing iron in the divalent state is titrated photometrically with 0.1000 N $\text{K}_2\text{Cr}_2\text{O}_7$. The following pairs of figures represent ab-

sorbances of the titrated solution after various volumes of $K_2Cr_2O_7$ have been added: .062, 32.00 ml; .064, 33.00 ml; .067, 34.00 ml; .069, 35.00 ml; .208, 36.00 ml; .381, 37.00 ml; .553, 38.00 ml. Plot the titration curve, and find the end-point volume of standard dichromate. How many milligrams of Fe(II) are in the sample? How would the titration curve be changed if the H_3PO_4 were left out?

Ans. 35.19 ml; 196.4 mg.

2. As in Eq. 22.2 (p. 541), 0.0100 M A is titrated with standard 0.100 M B. A and B are colorless, and the molar absorptivity of AB is 60 (moles/l) $^{-1}$ (cm) $^{-1}$. (a) Using Beer's law, calculate absorbances through a 1.00-cm cell for several points in the titration, assuming that the reaction between A and B is quantitative. (Do not calculate absorbances within 15% of the equivalence point, so that the extrapolation may be practiced without the aid of points near the equivalence point.) (b) Draw the titration curve and locate the end point. (c) Repeat the calculations of parts a and b, but with a standard solution containing 0.0100 M B, instead of 0.100 M B. (d) Explain the cause of curvature in the segments of the titration curve. How may such curvature be reduced to permit more precise location of the end point?

3. Repeat the calculations of Prob. 2, parts a and b, but with the original sample solution also containing an inert absorbing impurity that gives an initial absorbance of 0.600 to the solution before the titration is begun. Compare the titration curve with that of Prob. 2.

Experiment 22.1

1. For a particular sample and standard solution, V_1 is 26.53 mv and V_2 is 26.41 mv. What is the asymmetry potential of the electrode pair? *Ans.* 0.06 mv.

2. A diluted sample solution gives 13.96 mv when measured against a standard solution containing $6.0 \times 10^{-4} M$ chloride, the electrode in the sample solution being positive. If there is no asymmetry potential, what is the chloride concentration in the diluted sample solution?

3. A 0.000690 M sample solution is measured against a 0.000480 M standard solution. What are the voltage and the polarity of the electrode in the sample solution? *Ans.* 9.32 mv; negative.

4. In the following calculations, assume that the value of the Nernst constant is 0.05910, and ignore asymmetry potentials. (a) What is the chloride concentration in a diluted sample solution whose V against a 0.000400 M standard chloride solution is 5.74 mv? The sample electrode is negative. (b) Suppose that an instrumental error of 0.10 mv is made in measuring the voltage of part a, so that the voltage obtained is 5.84 mv. What is the calculated concentration of the sample, and what is its relative error, taking the value of part a as correct? (c) Repeat the calculation of part a, if the measured voltage is 64.84 mv. (d) Suppose that a 0.10-mv error is made in measuring the voltage of part c, so that the voltage obtained is 64.94 mv. What is the calculated concentration of the sample, and what is its relative error, taking the value of part c as correct?

Ans. (a) 0.000500 M ; (b) 0.000502 M , 0.4%;
(c) 0.00500 M ; (d) 0.00502 M , 0.4%.

Comparison of the answers to this problem indicates that a particular absolute error in V causes a particular relative error in X ; namely, a 0.1-mv error in V causes a 0.4% relative error in X .

Note that when A and X are fairly close to each other, as in part a, V is small (5.74 mv), and a tolerable error of 0.1 mv in V represents a rather large tolerable relative error of about 2% in V . Precise temperature control is not required to

measure V within such tolerances. On the other hand, when A and X are quite different, as in part c , V is large (64.84 mv), and a tolerable error of 0.1 mv in V represents a rather small tolerable relative error of only about 0.2%. Fairly good temperature control is required to measure V within such tolerances.

This problem should make clear the advantages of selecting a standard solution concentration that is of the same order of magnitude as the sample concentrations to be measured.

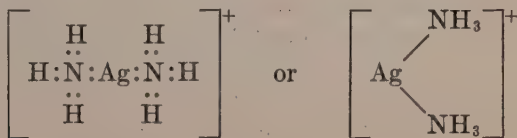
23 COMPLEXATION TITRATIONS

23A. COMPLEX FORMATION

23A.1. The Nature of Coordination Compounds

23A.1a. Definition. A *coordination compound* (or *complex*) is formed by the stoichiometric combination of molecules or ions which are themselves capable of independent existence. A few familiar examples are $\text{Ag}(\text{NH}_3)_2^+$, $\text{Fe}(\text{SCN})_6^{3-}$, AlF_6^{3-} .

A coordination compound consists of a metal ion (which is an electron *acceptor*), and a *donor* compound (which contains an atom with an unshared electron pair). The mutual attraction of the donor and acceptor for the electron pair bonds them together. Thus, in the complex, $\text{Ag}(\text{NH}_3)_2^+$, the Ag^+ is the electron acceptor, and shares a pair of electrons with each of two donor N-atoms in NH_3 . The electronic structure of the complex is symbolized.



23A.1b. Nature of the acceptor atom. Although a metallic ion has a stable electronic configuration, it may form additional completed shells by sharing electron pairs with donor atoms. The number of electron pairs that a metal ion may share in this way is called the *coordination number*, and is usually 4 or 6, but sometimes 2 or 8, depending on

the metal and its oxidation number, but independent of the nature of the donor atom. Thus, Zn^{2+} , which has the electronic configuration of 2, 8, 18, has a coordination number of 4, which when satisfied gives another stable configuration of 2, 8, 18, 8. A few complexes of Zn^{2+} are $\text{Zn}(\text{NH}_3)_4^{2+}$, $\text{Zn}(\text{OH})_4^-$, and ZnCl_4^- .

Other metal ions containing a complete or partially complete outer shell may expand to form a larger shell. Thus, Si(IV), which in SiF_4 has the electronic structure 2, 8, 8, acquires another stable structure of 2, 8, 12 in SiF_6^- . Still other metals form coordination compounds by both processes, i.e., both by enlarging an outer shell, and by forming an additional shell.

Virtually all of the metallic elements form complexes and have definite coordination numbers. Table 23.1 lists some common ions, their coordination numbers, and some typical complexes.

TABLE 23.1
COORDINATION NUMBERS OF SOME COMMON METAL IONS*

Ion	Coordination Number	Typical Complex	Ion	Coordination Number	Typical Complex
H^+	2	HF_2^-	Al^{3+}	6	AlF_6^-
Ag^+	2	$\text{Ag}(\text{NH}_3)_2^+$	Fe^{3+}	6	$\text{Fe}(\text{CN})_6^-$
B^{3+}	4	BF_4^-	Cr^{3+}	6	$\text{Cr}(\text{H}_2\text{O})_6^{3+}$
Zn^{2+}	4	$\text{Zn}(\text{NH}_3)_4^{2+}$	Co^{3+}	6	$\text{Co}(\text{NH}_3)_6^{3+}$
Cu^{2+}	4	$\text{Cu}(\text{NH}_3)_4^{2+}$	La^{3+}	6	$\text{La}(\text{C}_2\text{O}_4)_3^-$
Cd^{2+}	4	$\text{Cd}(\text{NH}_3)_4^{2+}$	Si^{4+}	6	SiF_6^-
Hg^{2+}	4	$\text{Hg}(\text{CN})_4^-$	Sn^{4+}	6	SnCl_6^-
Pt^{2+}	4	$\text{Pt}(\text{NH}_3)_4^{2+}$	Pb^{4+}	6	PbF_6^-
Fe^{2+}	6	$\text{Fe}(\text{CN})_6^{4-}$	Pt^{4+}	6	$\text{Pt}(\text{NH}_3)_6^{4+}$
Co^{2+}	6	$\text{Co}(\text{NH}_3)_6^{2+}$	Mo^{4+}	8	$\text{Mo}(\text{CN})_8^{4-}$
Ni^{2+}	6	$\text{Ni}(\text{NH}_3)_6^{2+}$	W^{4+}	8	$\text{W}(\text{CN})_8^{4-}$

*Reprinted from A. E. Martell and M. Calvin, *Chemistry of the Metal Chelate Compounds* (Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1952), Table 1.2, by permission of the publisher.

23A.1c. Nature of the donor atom. In aqueous solution, donors are limited entirely to strongly nonmetallic elements, particularly N, O, and S.

The molecule or ion containing the donor atom is called a *ligand*. Ligands are classified according to the number of donor atoms per ligand molecule. *Unidentate* ligands contain only one donor atom per molecule. *Multidentate* (i.e., bidentate, . . . , octadentate) ligands contain more than one donor atom per molecule.

Among the most common inorganic ligands are NH_3 , H_2O , OH^- , CN^- , SCN^- , halides, and PO_4^- . Potentially, all anions can be donors, but they vary in complexing strength. Thus, SO_4^- and NO_3^- have some

complexing ability, but they are generally weaker ligands than the above-mentioned groups. ClO_4^- apparently has a very low complexing tendency.

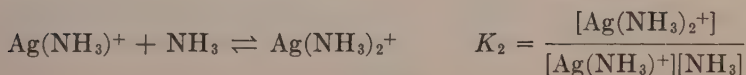
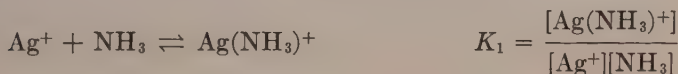
In organic ligands, there are several different kinds of coordinating groups. Among ligands with N-containing groups are amines, amides, Schiff base N, nitroso ($-\text{NO}$), azo ($-\text{N}=\text{N}-$), and cyanide ($-\text{CN}$). Alcoholic, phenolic, ether, keto oxygen, and analogous S-containing groups also show coordinating ability. In addition, groups that contain an ionizable hydrogen atom can coordinate with metal ions after the H^+ is split off. These are called *salt-forming groups*, but once formed, the coordinate bond is no different from that formed by the previously mentioned coordinating groups. Among the common salt-forming groups are: $-\text{COOH}$ (carboxyl), $-\text{OH}$ (alcoholic or phenolic), $-\text{COSH}$ (thiocarboxy), $-\text{SH}$ (mercapto), $=\text{NOH}$ (oxime), $=\text{NH}$ (imine).

23A.2. Stability of Coordination Compounds

In aqueous solution, the coordination valencies of a metal ion are always filled, either by water or by other electron-pair donors that may be present. Thus, unhydrated Ag^+ is incapable of independent existence in aqueous solution: $\text{Ag}(\text{H}_2\text{O})_2^+$ is the predominant species. When other donors are present, other complex ions are conceived to be formed by the displacement of water from the coordination sphere. Thus, as the concentration of NH_3 increases, it may displace H_2O stepwise from the coordination sphere of Ag^+ :



For simplicity, water of coordination is usually omitted from complexation equations, and the above equations may be written:



The equilibrium constants K_1 and K_2 are called *stability constants*, and are larger the more stable the complexes. The reciprocals of K_1 and K_2 (for the reverse, or dissociation reactions) are called *instability constants* or *dissociation constants*.

For some purposes, combinations of the stepwise stability constants are used. Thus, in the presence of a large excess of NH_3 , where

$\text{Ag}(\text{NH}_3)_2^+$ is the predominant Ag^+ -bearing species, the over-all reaction suffices, its equilibrium constant being the product of the stepwise constants.



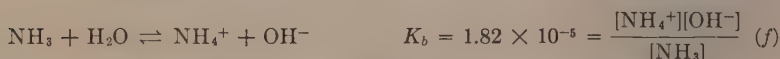
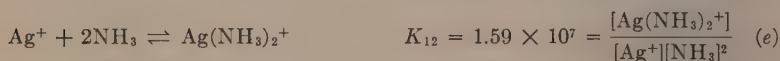
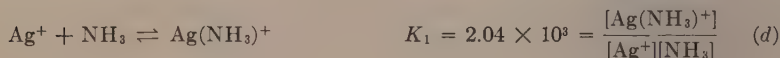
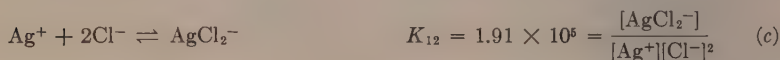
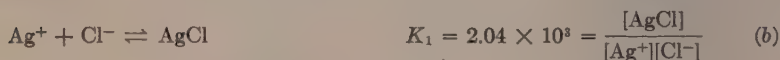
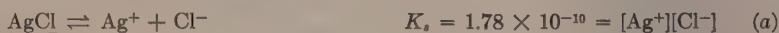
Appendix X is an abbreviated list of stability constants pertinent to topics and problems in this text. A more extensive table has been compiled (B13).

Because several intermediate complexes may be formed between a given metal ion and a given ligand, the stability constants are usually difficult to measure, and are not known precisely. Also, some complexes are only formed in concentrated solutions, where activity effects are large and poorly known, especially for multiply-charged ions. Therefore, calculations that involve complex ion equilibria are usually not very accurate.

Methods for the determination of stability constants have recently been summarized (R15).

Example 1. Calculate the solubility of AgCl in $0.10\text{ }M\text{ NH}_3$.

Inspection of Appendices V, VIIA, and X gives the equilibrium constants for the following pertinent equilibria:



This system of equations is far too complicated to solve rigorously. However, inspection of the magnitudes of the equilibrium constants indicates that the method of the principal equilibrium is applicable. Since the ammonia concentration is relatively high, and since the equilibrium constant for reaction *e* is relatively large, the silver in solution is probably predominantly in the form $\text{Ag}(\text{NH}_3)_2^+$, in which case the principal equilibria are *a* and *e*. Proceeding on this assumption, and letting *x* be the molar solubility of AgCl ,

$$[\text{Cl}^-] = [\text{Ag}(\text{NH}_3)_2^+] = x \quad (g)$$

Since K_b is so small, it can safely be assumed that NH_3 is inappreciably ionized, in which case

$$[\text{NH}_3] = 0.10 - 2x \quad (h)$$

The four equations a , e , g , and h may be solved for x to give

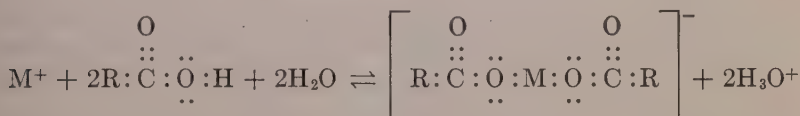
$$1.59 \times 10^7 = \frac{x^2}{1.78 \times 10^{-10}(0.10 - 2x)^2} \quad (i)$$

$$x, \text{ or the molar solubility of } \text{AgCl} = 0.0048 M \quad (j)$$

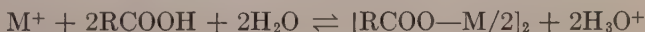
The assumption made in obtaining the answer may be tested. If the concentrations of all other Ag^+ -bearing species are calculated, they prove to be negligible compared to $[\text{Ag}(\text{NH}_3)_2^+]$, or $0.0048 M$, justifying the assumption. Typically, $[\text{Ag}^+]$ may be found from Eqs. a , g , and j :

$$[\text{Ag}^+] = \frac{1.78 \times 10^{-10}}{0.0048} = 3.7 \times 10^{-8} M$$

By way of illustrating the structure of organic complexes, M^+ (a metal ion with coordination number 2) might form a complex with an organic acid as follows:

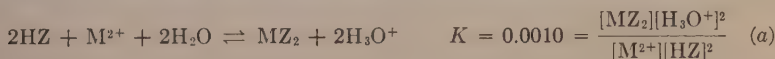


Generally, only the electrons in the coordinate bond are shown, each pair being symbolized with a dash:



Equilibria involving metal-organic complexes are also characterized by definite equilibrium constants (B13). The organic systems are generally more complicated than inorganic ones, because many organic ligands are also weak acids or bases, and their complexing efficiency depends on the $p\text{H}$, as shown in the following example.

Example 2. A solution contains $0.010 M$ HZ (a weak acid whose K_a is 2.0×10^{-5}), and $1.0 \times 10^{-5} M$ MCl_2 . Assume that only a single complex MZ_2 is formed:



Calculate the ratio of complexed to uncomplexed M^{2+} (i.e., $[\text{MZ}_2]/[\text{M}^{2+}]$) in solutions buffered at (a) $p\text{H}$ 5.00, (b) $p\text{H}$ 2.00.

At $p\text{H}$ 5.00, or $[\text{H}_3\text{O}^+] = 1.00 \times 10^{-5} M$, $[\text{HZ}]$ may be calculated from the ionization-constant expression.

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{Z}^-]}{[\text{HZ}]} \quad (b)$$

$$2.0 \times 10^{-5} = \frac{(1.0 \times 10^{-5})(0.010 - [\text{HZ}])}{[\text{HZ}]} \quad (c)^*$$

$$[\text{HZ}] = 0.0033 \text{ M} \quad (d)$$

From Eq. *a*,

$$\frac{[\text{MZ}_2]}{[\text{M}^{2+}]} = K \frac{[\text{HZ}]^2}{[\text{H}_3\text{O}^+]^2} = 0.0010 \frac{(0.0033)^2}{(1.0 \times 10^{-5})^2} = 110 \text{ (pH 5)} \quad (e)$$

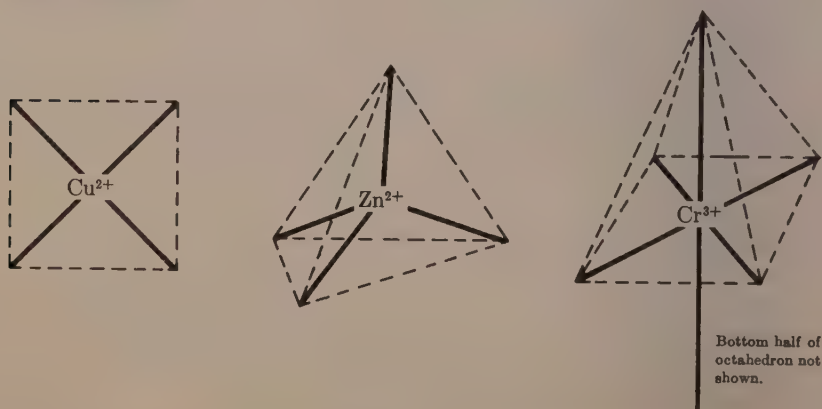
At pH 2.00, the acidity is high enough to put all of the complexing agent into the undissociated form, and $[\text{HZ}]$ is very close to 0.010 M. From Eq. *a*,

$$\frac{[\text{MZ}_2]}{[\text{M}^{2+}]} = K \frac{[\text{HZ}]^2}{[\text{H}_3\text{O}^+]^2} = 0.0010 \frac{(0.010)^2}{(0.010)^2} = 0.0010 \quad (f)$$

Comparison of Eqs. *e* and *f* shows that M^{2+} passes from an almost quantitatively complexed condition to a quantitatively uncomplexed condition when the pH is lowered from 5 to 2. Such behavior is typical of many metal-organic complexes. The ability to control the extent of complexing through control of pH is of great analytical use.

23A.3. Structure of Coordination Compounds

The coordination valencies are directed about the central atom, just as are the primary chemical valencies, in a way that depends upon the metal atom and its oxidation number. The coordinated ligands are therefore geometrically arranged about the acceptor atom. For example, the bonds about some metal ions with coordination number 4 (like Cu^{2+}) are *planar*, while others (like Zn^{2+} and Cd^{2+}) are *tetrahedral*. Many metal ions with coordination number 6 (like Cr^{3+}) have an *octahedral* structure:



* $[\text{Z}^-]$ may be expressed in terms of $[\text{HZ}]$, using a material balance on the total ligand concentration

$$0.010 = [\text{Z}^-] + [\text{HZ}] + 2[\text{MZ}_2]$$

↑ Negligible, since the total M concentration is low.

$$[\text{Z}^-] = 0.010 - [\text{HZ}]$$

In the complexes, the geometrical structures are not always regularly symmetrical; there is usually some distortion caused by the ligands as they fit into the coordination sphere of the metal atom. Generally, the greater the distortion, the less stable is the complex. If the distortion required to accommodate a particular ligand is too great, the complex is so unstable that it does not form appreciably.

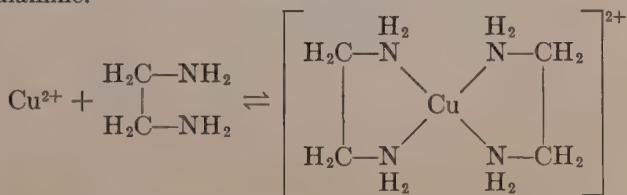
Sometimes, the complexes that form may be limited by geometrical (i.e., steric) factors. If the ligands are too large, not enough of them may be able to fit into the coordination sphere of the metal ion to fill all of its coordination valencies. In such a case, only a fraction of the coordinate valencies may be filled by the large ligands, and the residual valencies must be filled by smaller ligands or water. Also, a ligand may contain a structure or groups in the vicinity of the donor atom that hinder it from approaching closely enough to the acceptor atom to form the bond.

23A.4. Rates of Complexation Reactions

Although many complexing reactions occur very rapidly, some occur very slowly. Failure to consider the rate of a complexing reaction may lead to erroneous conclusions about the stability of the complex. For instance, very little CrSCN^{2+} is formed on adding 0.1 *M* KSCN to 0.1 *M* $\text{Cr}(\text{ClO}_4)_3$, even after several hours at room temperature. From this experiment, one might conclude that CrSCN^{2+} is an unstable complex. Actually, it is as stable a complex as FeSCN^{2+} , which forms immediately after mixing KSCN and $\text{Fe}(\text{ClO}_4)_3$, but the rate of formation of the chromium complex is very low at room temperature. If the solution is heated for a few hours at 90°C, CrSCN^{2+} is formed quantitatively, and remains on cooling the system to 25°C.

23A.5. Chelate Compounds

A single multidentate molecule may satisfy more than one coordinate valency on a metal atom, so that a ring or *chelate structure* of atoms may be formed. Many metal-organic complexes are of this type. A simple example is the complex between quadrivalent Cu(II) and bidentate ethylenediamine.




Rings with 5 or 6 atoms in them are the most stable, because the bond angles of the constituent atoms are least distorted. The strain and in-

stability increase rapidly as the number of atoms in the ring decreases below 5. On the other hand, two coordinating groups widely separated on a ligand chain are kept physically apart by the intervening chain; the longer the chain, the less the likelihood that both groups will coordinate with the same metal ion (**B1**).

Also, the greater the number of 5- or 6-membered rings that a chelating molecule may form with a particular metal ion, the greater is the stability of the chelate (**S7**). Table 23.2 gives stability constants for several nickel ammine complexes, and it may be seen that the stabilities increase by several orders of magnitude for each additional ring that is formed. Table 23.3 shows the increase in complexing ability as H-atoms of NH_3 are replaced by acetate groups, which permit chelation to occur.

Stability constants for many chelate compounds have been compiled (**B13**).

TABLE 23.2
STABILITY CONSTANTS FOR NICKEL AMMINE COMPLEXES*†

Complexing Agent □ = basic nitrogen ● = carbon		Logarithms of Stepwise Stability Constants					
Ammonia NH ₃	□	2.8	2.2	1.7	1.2	0.7	-0.01
Ethylenediamine	H ₂ N—CH ₂ —CH ₂ —NH ₂ □ — ● — ● — □	7.7		6.5		5.1	
1,3-diaminopropane	H ₂ N—CH ₂ —CH ₂ —CH ₂ —NH ₂ □ — ● — ● — ● — □	6.4		4.3		1.2	
Diethylenetriamine		10.7			8.3		
1, 2, 3-triaminopropane	□ — ● — ● — ● — □ 						

*Reprinted from G. Schwarzenbach, *Analyst*, 80, 713 (1955), Table 2, by permission of The Society for Analytical Chemistry.

†Temperature, 20°C; ionic strength, 0.1.

TABLE 23.3
STABILITY CONSTANTS OF 1:1 ZN COMPLEXES*†

Complexing Group and Formula	Log of Stability Constant
Ammonia, NH_3	2.27
Aminoacetate, $\text{NH}_2\text{—CH}_2\text{—COO}^-$	4.80
Iminodiacetate, $\text{NH}(\text{CH}_2\text{—COO})_2^-$	7.77
Nitrilotriacetate, $\text{N}(\text{CH}_2\text{—COO})_3^-$	10.45
Ethylenediamine-tetraacetate $\left[\begin{array}{c} \text{CH}_2\text{—N}(\text{CH}_2\text{—COO})_2 \\ \\ \text{CH}_2\text{—N}(\text{CH}_2\text{—COO})_2 \end{array} \right]^{4-}$	16.12

*Reprinted from G. Schwarzenbach, *Analyst*, 80, 713 (1955), Table 3, by permission of The Society for Analytical Chemistry.

†Temperature, 20°C; ionic strength, 0.1.

The coordination number of the metal ion determines the maximum number of complexing molecules that can combine with the metal. Thus, a metal ion with coordination number 6 may hold 3 bidentate molecules (a), 2 tridentates (b), or one sexidentate molecule (c).



(a) Bidentate complexer
X X



(b) Tridentate complexer
X X



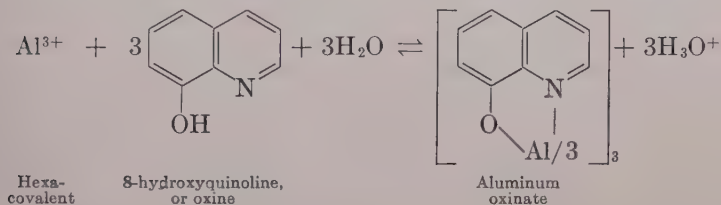
(c) Sexidentate complexer



(d) Mixed complex

Mixed complexes may form if more than one complexer is present, or if the maximum number of complexer molecules cannot fit into the coordination sphere of the metal ion, or if not enough complexer molecules of a particular kind are present. Thus, complexes like (d) may be formed, where X_3 is a tridentate complexer, and Z may be H_2O , OH^- , or donor groups on other complexers. In any given solution, there may be several such complexes present, the proportion of each being dependent upon the composition of the solution and the stability constants of the various complexes. For instance, in solutions where $[\text{X}_3]:[\text{M}]$ is high,

Complexers that possess a salt-forming group for each coordination group form neutral complexes.



In general, charged complexes are soluble in water and insoluble in organic solvents. The neutral complexes are insoluble in water, but tend to be soluble in organic solvents. These solubility properties are used widely in performing analytical separations.

23B. ANALYTICAL APPLICATIONS OF COMPLEXATION REACTIONS

The applications of complexation reactions to analytical problems are many and varied. But for a few exceptions, however, they may be put into three classes: (1) control of chemical properties, (2) formation of colored compounds, (3) complexation titrations. The first two classes are discussed briefly in this section. Complexation titrations are discussed in detail in the following section.

23B.1. Control of Chemical Properties. Separations

The activity of a chemical species may be greatly reduced by complexing it. Complexation therefore offers a way of displacing chemical equilibria and of diminishing the effect of interferences without the actual physical removal of chemical species from the system, as shown in the following examples.

Example 1. The effect of an interference may often be reduced (i.e., *masked*) simply by complexing it. A familiar example is the diminution of the interference of Fe(III) in the spectrophotometric determination of Mn as permanganate. The interfering yellow color of hydrated Fe(III) is eliminated by conversion to colorless $\text{Fe}^{3+}\text{-PO}_4^{3-}$ complexes (p. 528).

Example 2. Redox potentials may be greatly affected by complexing agents. Thus, in the iodimetric determination of Cu(II), Fe(III) interferes because it is strong enough to oxidize I^- . By complexing Fe(III) into an FeF_6^{3-} complex, its oxidizing power is diminished sufficiently to prevent oxidation of the I^- (p. 489).

Example 3. Complexers may be of great use in separations. For example, even though CdS is much more soluble than CuS, CdS may be precipitated in the presence

of Cu(II), provided that CN^- is added to complex the Cu(II) as $\text{Cu}(\text{CN})_4^-$. Analogous examples apply to separation by solvent extraction, ion exchange, and electrodeposition.

Example 4. Some metal-organic chelates have very low solubilities in water. Some are stable, easily purified, and make good weighing forms for gravimetric analysis. A particular advantage of organic precipitants is that the solubility of the complex may be controlled with pH. As an example, oxine may be used as a precipitant for many metal ions. The dependence of solubility upon acidity is clearly shown in the equation on page 563. The common metals fall roughly into four groups, depending upon the pH that is required for complete precipitation.

1. Metals precipitating below pH 3: Cu, Fe, Ga, Pd.
2. Metals precipitating at pH 4–5: Al, Bi, Cd (pH 5.4), Co, In, Mo (pH 3.6), Ni, Th, Ti, Tl, U, V, W, Zn, Zr.
3. Metals precipitating at pH 6–7: Sb, Mn, Nb, Sc.
4. Metals precipitating above pH 8: Ca, Ce, Cr, Mg, Pb.

Generally, two metals may be separated by precipitation with oxine if they fall in different groups.

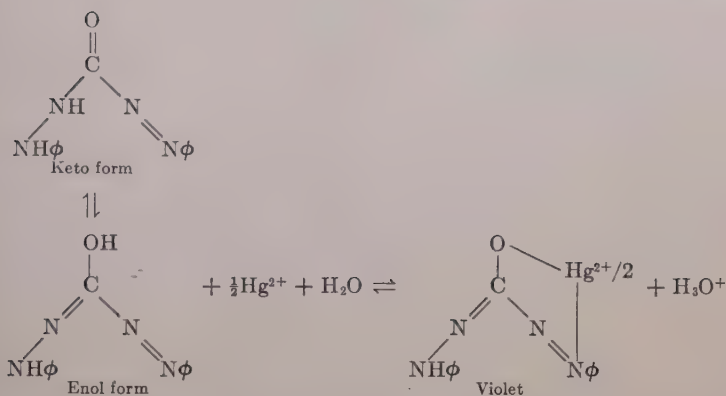
23B.2. Formation of Colored Compounds

When coordination occurs, the electronic structures of both the metal ion and complexer are changed, and the absorption of light by the complex may be different from that of the uncomplexed metal ion. The effect may be profound, and the absorbance may be very high in chelate structures that involve conjugated double bonds or chromophoric groups. The color of complexes is utilized in both qualitative and quantitative analysis.

23B.2a. Qualitative analysis. Tests for the qualitative detection of many organic and inorganic substances depend on color-forming reactions. Many *spot tests* exist that require only drop-size (0.05 ml) samples or less, and that permit detection of traces down to submicrogram levels, at concentrations of the order of 0.01 to 0.1 p.p.m. For the most part, the colored chelates are insoluble in water. In the spot tests, however, the colors of the complexes are noticeable at concentrations far below their solubility limits, which are not exceeded if the concentration of the sought-for substance is very low.

In a qualitative test with a particular complexer, still other complexers may find wide use as masking agents to eliminate interferences. The proper combination of color former, masking agent, and pH often permits a rather specific test for a particular substance in the presence of many other substances, as shown in the following example.

Example. Diphenyl carbazone forms a deep violet chelate with Hg(II), which is insoluble even in strongly acid solution:



Many other metals form such complexes in weakly acid or alkaline solution, but only the salt of Hg(II) is stable enough to persist in 0.2 *M* HNO₃. Molybdate and chromate interfere in acid solution to give colored compounds of an unknown nature. Mo(VI) may be masked with oxalic acid to form very stable and colorless oxalate complexes, and Cr(VI) may be reduced to nonreactive Cr(III), permitting a very specific test for Hg(II).

23B.2b. Spectrophotometric determinations. Many colored complexes are reproducible and stable enough to permit their spectrophotometric determination. The solubility of chelates in organic solvents may be utilized to permit measurement of the absorbance in nonaqueous solutions.

The typical organic reagent forms complexes with a number of metal ions, and is in this sense rather unselective. However, the different metal complexes may differ greatly in stability, thereby permitting some selectivity, as shown in the following example. Masking agents may also be employed to increase the selectivity further.

Example. A dilute solution of dithizone in chloroform is greenish, but when shaken with an aqueous solution of a complexable metal ion, the metal ion is taken into the chloroform phase as a violet, yellow, orange, or red complex. Many heavy metal ions form dithizonates, but only the dithizonates of Pd, Au, Hg, Ag, and Cu are stable enough to be extractable from acid solution. Further selectivity may be achieved within this small group with the proper masking agents. Thus, if Br⁻ (masks Pd, Au, and Cu) and SCN⁻ (masks Hg, Au, and Cu) are added to the acid solution, only the Ag complex remains extractable, and the determination is specific for Ag (S2).

23C. COMPLEXATION TITRATIONS

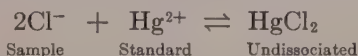
A *complexation titration* is one in which a soluble, undissociated, stoichiometric complex is formed at the equivalence point. In general, the coprecipitation errors associated with precipitation titrations are

nonexistent. In addition, many metals can be determined with a single chelating titrant (see Fig. 23.7, p. 589), selectivity among the metals being achievable to some extent by control of the pH at which the titration is performed.

23C.1. Titrations with Unidentate Complexers

Following are two well-known titrations with unidentate complexers.

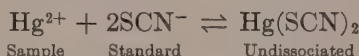
Titration of chloride with standard $Hg(NO_3)_2$.



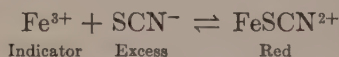
Suitable indicators are sodium nitroprusside ($Na_2Fe(CN)_5NO$), which forms a white precipitate with excess Hg^{2+} after the equivalence point, and diphenyl carbazone, which gives a violet color (see p. 571). The end point may be determined potentiometrically also.

A particular advantage is that Cl^- may be determined by direct titration with a visual indicator in acid solution. Br^- and I^- may be similarly titrated.

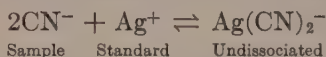
A related method is the titration of $Hg(II)$ with standard $KSCN$, also performable in acid solution.



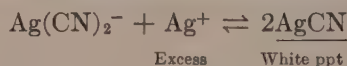
The indicator is $Fe(III)$, which reacts with the first excess of SCN^- past the equivalence point.



Titration of cyanide with standard $AgNO_3$ (Liebig method).



In theory, the first slight excess of $AgNO_3$ past the equivalence point precipitates white $AgCN$, which provides the end-point signal:



This procedure, however, is not practical, since some $AgCN$ is formed locally, and does not redissolve readily on stirring.

A practical indicator is KI in ammoniacal solution. The NH_3 prevents precipitation of $AgCN$, and the end-point signal is the formation of AgI , which is insoluble even in NH_3 . Any AgI formed locally before the equivalence point redissolves readily in the NH_3 solution. NH_3

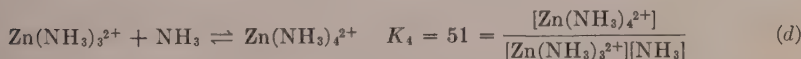
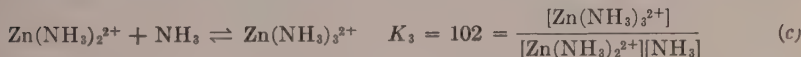
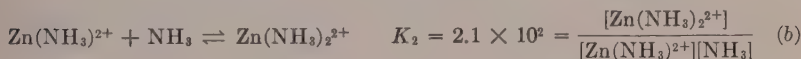
does not interfere with formation of the very stable $\text{Ag}(\text{CN})_2^-$ complex.



The Liebig method is a basis for the indirect titration of Ni, Co, Zn, and Cu, all of which form very stable cyanide complexes.

With the few exceptions noted in the previous section, almost all titrations based on unidentate complexers are unfeasible. Since the stepwise stability constants do not differ greatly, the metal ion is not quantitatively converted to a single stoichiometric complex at the equivalence point, and the titration curve shows no sharp inflection. The behavior of $\text{Zn}(\text{II})$ is typical, as described in the following example.

Example. Calculate the concentrations of the various Zn-bearing species in a solution made by mixing 50.00 ml of 0.100 *M* ZnCl_2 and 50.00 ml of 0.400 *M* NH_3 . (This is a solution resembling that at the equivalence point in the titration of $\text{Zn}(\text{II})$ with "standard" NH_3 .)



Eqs. *a-d* constitute four equations in six unknowns. The two additional equations required for solving may be obtained from material balances on Zn^{2+} and NH_3 :

$$0.0500 = [\text{Zn}^{2+}] + [\text{Zn}(\text{NH}_3)^{2+}] + [\text{Zn}(\text{NH}_3)_2^{2+}] + [\text{Zn}(\text{NH}_3)_3^{2+}] + [\text{Zn}(\text{NH}_3)_4^{2+}] \quad (e)$$

$$0.200 = [\text{NH}_3] + [\text{Zn}(\text{NH}_3)^{2+}] + 2[\text{Zn}(\text{NH}_3)_2^{2+}] + 3[\text{Zn}(\text{NH}_3)_3^{2+}] + 4[\text{Zn}(\text{NH}_3)_4^{2+}] \quad (f)$$

Eqs. *a-d* may be used to eliminate all complex concentrations except $[\text{Zn}^{2+}]$ and $[\text{NH}_3]$ from Eqs. *e* and *f*. For brevity, let $[\text{Zn}^{2+}] = x$ and $[\text{NH}_3] = y$.

$$[\text{Zn}(\text{NH}_3)^{2+}] = K_1xy \quad (g)$$

$$[\text{Zn}(\text{NH}_3)_2^{2+}] = K_1K_2xy^2 \quad (h)$$

$$[\text{Zn}(\text{NH}_3)_3^{2+}] = K_1K_2K_3xy^3 \quad (i)$$

$$[\text{Zn}(\text{NH}_3)_4^{2+}] = K_1K_2K_3K_4xy^4 \quad (j)$$

$$0.0500 = x + K_1xy + K_1K_2xy^2 + K_1K_2K_3xy^3 + K_1K_2K_3K_4xy^4 \quad (k)$$

$$0.200 = y + K_1xy + 2K_1K_2xy^2 + 3K_1K_2K_3xy^3 + 4K_1K_2K_3K_4xy^4 \quad (l)$$

Eqs. *k* and *l* may be used to eliminate *x*, giving an equation in *y* alone that is solvable by trial and error.

$$K_1K_2K_3K_4y^5 + K_1K_2K_3y^4 + (K_1K_2 - 0.0500K_1K_2K_3)y^3 + (K_1 - 0.100K_1K_2)y^2 + (1 - 0.150K_1)y - 0.200 = 0 \quad (m)$$

$$4.26 \times 10^3y^5 + 8.36 \times 10^3y^4 - 33.6 \times 10^4y^3 - 78.1 \times 10^2y^2 - 57.5y - 0.200 = 0 \quad (n)$$

$$y, \text{ or } [\text{NH}_3] = 0.0306 M \quad (o)$$

$$x, \text{ or } [\text{Zn}^{2+}] = 7.1 \times 10^{-5} \quad (p)$$

The complex ion concentrations may be found by substituting Eqs. *o* and *p* into Eqs. *g-j*.

$$[\text{Zn}(\text{NH}_3)^{2+}] = 0.00085 M$$

$$[\text{Zn}(\text{NH}_3)_2^{2+}] = 0.0054 M$$

$$[\text{Zn}(\text{NH}_3)_3^{2+}] = 0.0170 M$$

$$[\text{Zn}(\text{NH}_3)_4^{2+}] = 0.0265 M$$

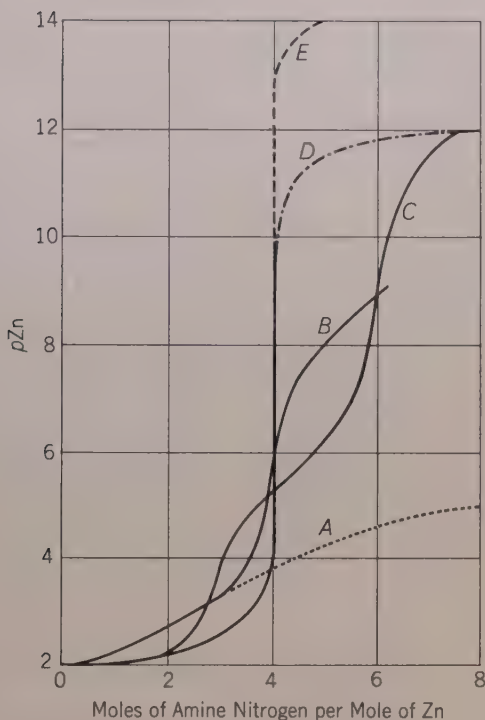
It may be seen that even though there are four moles of NH_3 per mole of $\text{Zn}(\text{II})$, the species $[\text{Zn}(\text{NH}_3)_4^{2+}]$ is far from being predominant. Likewise, it may be shown that no one species is predominant at any of the points corresponding to 1, 2, or 3 moles of NH_3 per mole of $\text{Zn}(\text{II})$, and the titration of $\text{Zn}(\text{II})$ with NH_3 is not at all feasible. (See Fig. 23.1.)

23C.2. Multidentate Titrants Compared with Unidentate Titrants

In the case of a multidentate complexer, not only is the number of steps decreased but the differences between the stepwise stability constants are larger than for unidentate complexers. (See Tables 23.2, 23.3.) When the complexing molecule possesses enough ligands to fill the whole coordination sphere of the metal ion, then only one stable complex is formed, and the titration curve has a single steep inflection region. These generalizations are illustrated in Fig. 23.1, which gives curves for the titration of $\text{Zn}(\text{II})$ with various complexing agents. Note that the titration with NH_3 is completely unfeasible, while the steepness and range of the inflection region both increase as the number of ligands per molecule of complexer increases.

23C.3. Titrations with EDTA (F5, R6)

23C.3a. Structure and properties of EDTA. One of the most versatile of complexation titrants is ethylenediaminetetraacetic acid (EDTA, or H_4Y), which has the following special advantages. (1) It forms very stable, soluble, stoichiometric, 1:1 complexes with many metal ions. (2) Since the stability constants of the various metal ion complexes



Curve	Titrating Agent and Formula □ = basic nitrogen; ● = carbon	Log of Stepwise Stability Constants
A	Ammonia, □	2.3, 2.4, 2.4, 2.1
B	Ethylenediamine, □—●—●—□	5.9, 5.2
C	Diethylenetriamine, □—●—●—□—●—●—□	8.9, 5.5
D	Triethylenetetramine, □—●—●—□—●—●—□—●—●—□	12.1
E	Triaminotriethylamine, <div style="display: inline-block; vertical-align: middle;"> <div style="display: inline-block; vertical-align: middle;">●—●—□</div> <div style="display: inline-block; vertical-align: middle;">□—●—●—□</div> <div style="display: inline-block; vertical-align: middle;">●—●—□</div> </div>	14.7

FIG. 23.1. Titration of Zn(II) with Amines (Reprinted from G. Schwarzenbach, *Analyst*, 80, 713 [1955], Fig. 3, by permission of The Society for Analytical Chemistry.)

vary widely (see Table 23.4), some selectivity among various cations may be obtained simply by controlling the pH at which the titration is performed. (3) The disodium salt of EDTA is an acceptable primary standard. (4) Since the metal complexes are soluble, coprecipitation

TABLE 23.4

LOGS OF STABILITY CONSTANTS OF 1:1 METAL ION CHELATES*†

Chelating Agent: Metal Ion	Trien	Tetren	NTA	EDTA	HEDTA	EEDTA	EGTA	DTPA	CDTA
Mg ²⁺	nil	nil	5.4	8.7	7.0	8.3	5.4	9.0	10.3
Ca ²⁺	nil	nil	6.4	10.7	8.0	10.0	10.9	10.7	12.3
Sr ²⁺	nil	nil	5.0	18.7	6.8	8.6	8.5	9.7	10.0
Ba ²⁺	nil	nil	4.8	7.9	6.2	8.2	8.4	8.6	8.0
La ³⁺	nil	nil	10.4	15.5	13.2			19.1	
R.E.			10.4–12.2	15.8–19.8	14.1–15.8				16.8–21.5
Mn ²⁺	4.9	7.0	7.4	13.8	10.7	13.2	12.3	15.5	16.8
Fe ²⁺	7.8		8.8	14.4	11.6			16.7	
Fe ³⁺			15.8	25.1				27.5	
Co ²⁺	11.0	15.1	10.4	16.3	14.4	14.7	12.3	19.0	18.9
Ni ²⁺	14.0	17.8	11.5	18.6	17.0	14.7	13.6	20.2	19.4
Cu ²⁺	20.1	22.9	12.6	18.8	17.4	17.8	17.8	21.0	21.3
Zn ²⁺	11.9	15.4	10.5	16.5	14.5	15.3	13.0	18.8	18.6
Cd ²⁺	10.8	14.0	9.8	16.5	13.0	16.3	16.7	19.0	19.2
Hg ²⁺	25.0	27.7		22.1	20.1	23.1	23.8	27.0	24.4
Al ³⁺	nil	nil		16.1					17.6
Pb ²⁺	10.4	10–11	11.1	17.9	15.5	14.4	14.6	18.6	19.7

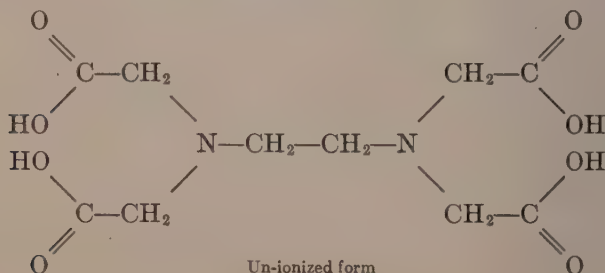
*Reprinted from C. N. Reilley, R. W. Schmid, and F. S. Sadek, *Journal of Chemical Education*, 36, 555 (1959), Table 3, by permission of the publisher.

†Chelate formation reaction: $M^{m+} + Z^{s-} \rightleftharpoons MZ^{m-s}$

‡See Table 23.5 for names, formulae, and acid ionization constants of the chelating agents.

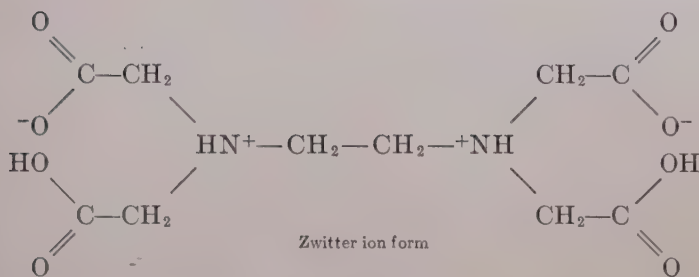
errors are nonexistent. (5) The equivalence point may be found in a variety of ways.

EDTA is a sexidentate complexer:



In solution, the acid itself exists as a double zwitter ion, and the first two protons are rather easily removed ($pK_1 = 2.18$; $pK_2 = 2.73$). The third and fourth protons are weakly ionized ($pK_3 = 6.20$; $pK_4 = 10.0$). (See Table 23.5, p. 578.)

The dihydrate of the disodium salt, $Na_2H_2Y \cdot 2H_2O$ (MW, 372.24), is commercially available in reagent grade, and is easy to purify, store,



and use as a primary standard. The disodium salt is commonly used in reagent solutions because the acid is quite insoluble in water. Stored in plastic bottles, standard $\text{Na}_2\text{H}_2\text{Y}$ solutions are very stable for many months. Stored in glass bottles, however, the titer may decrease by several per cent per month, because metal ions are leached from the glass.

Since it is the anion, Y^{4-} , that chelates with metal ions, protons are liberated when complexing occurs, and the extent of complex formation may be regulated by adjusting the pH . Thus, the reaction between $\text{Na}_2\text{H}_2\text{Y}$ and the metal M^{m+} is



For most metal ions, the 1:1 complex is formed predominantly over a wide range of conditions. The 1:1 complexes are extremely stable because all coordination valencies on a metal ion up to 6 may be satisfied by a single molecule of Y^{4-} . The structure of the 1:1 complex with hexavalent Ca^{2+} is

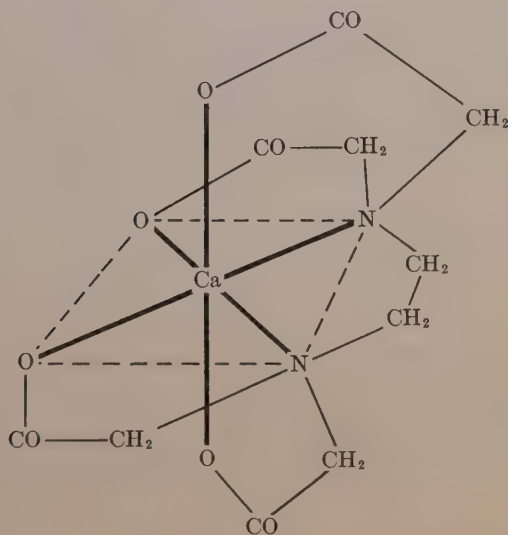


TABLE 23.5

CHELATING TITRANTS*

Chelating Agent	Symbol	Formula of Completely Deprotonated Form	pK_1	pK_2	pK_3	pK_4	pK_5
Triethylenetetramine	Trien	$\begin{array}{c} \text{CH}_2\text{—NH—CH}_2\text{—CH}_2\text{—NH}_2 \\ \\ \text{CH}_2\text{—NH—CH}_2\text{—CH}_2\text{—NH}_2 \end{array}$	3.32	6.67	9.20	9.92	
Tetraethylenepentamine	Tetren	$\begin{array}{c} \text{CH}_2\text{—CH}_2\text{—NH—CH}_2\text{—CH}_2\text{—NH}_2 \\ \\ \text{CH}_2\text{—CH}_2\text{—NH—CH}_2\text{—CH}_2\text{—NH}_2 \end{array}$	2.6	4.1	8.2	9.2	10.0
Nitrilotriacetic acid, or ammoniatriacetic acid	NTA	$\begin{array}{c} \text{CH}_2\text{—COO}^- \\ \\ \text{—OOC—CH}_2\text{—N—CH}_2\text{—COO}^- \end{array}$	1.9	2.49	9.73		
Ethylenediaminetetraacetic acid	EDTA	$\begin{array}{c} \text{CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \end{array}$	2.18	2.73	6.20	10.0	
N-Hydroxyethylethylenediaminetetraacetic acid	HEDTA	$\begin{array}{c} \text{CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \\ \\ \text{HOCH}_2\text{—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \end{array}$	2.64	5.33	9.73		
Ethylenetherdiaminetetraacetic acid	EEDTA	$\begin{array}{c} \text{CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \\ \\ \text{HOCH}_2\text{—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \end{array}$	1.90	2.67	8.82	9.49	
Ethylene glycol-bis-(β -aminoethyl ether)-N,N'-tetraacetic acid	EGTA	$\begin{array}{c} \text{CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—O—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \end{array}$	2.0	2.68	8.85	9.43	
Diethylenetriamine-pentaacetic acid	DTPA	$\begin{array}{c} \text{CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—CH}_2\text{—N—CH}_2\text{—COO}^- \end{array}$	2.03	2.41	4.27	8.60	10.55
Cyclohexanediaminetetraacetic acid	CDTA	$\begin{array}{c} \text{CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—COO}^- \\ \\ \text{—OOC—H}_2\text{C—N—CH}_2\text{—CH}_2\text{—COO}^- \end{array}$	2.40	3.52	6.12	11.70	

*Reprinted in part from C. N. Reilley, R. W. Schmid, and F. S. Sadek, *Journal of Chemical Education*, 36, 555 (1959), Table 2, by permission of the publisher.

23C.3b. EDTA titration curves. If a solution of a metal ion, M^{m+} , is titrated with a standard $\text{Na}_2\text{H}_2\text{Y}$ solution, the metal ion concentration decreases as the titration proceeds, and pM increases. If the stability of the MY^{m-4} complex is sufficiently great, and if the acidity of the solution is sufficiently low to permit quantitative formation of the complex at the equivalence point, then pM will increase sharply in the region of the equivalence point. A plot of pM against milliliters of standard $\text{Na}_2\text{H}_2\text{Y}$ gives an S-shaped titration curve similar to an ordinary pH titration curve. Typical pM titration curves are shown in Fig. 23.2, with points on the curves being calculated as in the following example.

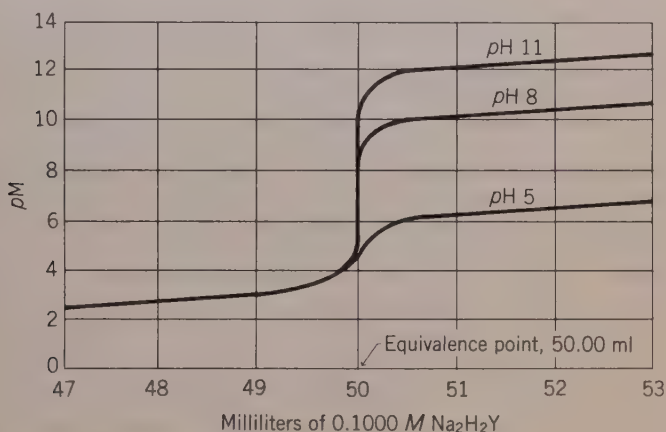


FIG. 23.2. Titration of MCl_2 with $\text{Na}_2\text{H}_2\text{Y}$ —Conditions: (1) 50.00 ml of 0.1000 M MCl_2 titrated with 0.1000 M $\text{Na}_2\text{H}_2\text{Y}$. (2) Ionization constants for H_4Y are rounded to simplify computation: $pK_1 = 2.00$, $pK_2 = 3.00$, $pK_3 = 6.00$, $pK_4 = 10.00$. (3) Stability constant for MY^- , 14.00. (4) pH buffered as shown on curves. (5) It is assumed that volumes are additive, activity effects are negligible, and that MY^- is the only complex formed.

Example. Calculate pM when the following volumes of 0.1000 M $\text{Na}_2\text{H}_2\text{Y}$ are added to 50.00 ml of 0.1000 M MCl_2 , at pH 5.00, and under the conditions enumerated in Fig. 23.2: (a) 50.20, (b) 50.00 (eq. pt.), (c) 49.70 ml.

In problems of this sort, where a pH buffer is used to control a chelating ion concentration (like EDTA), only a fraction of the uncomplexed EDTA (U M) exists as Y^{4-} , the rest being bound into various protonated forms. At a particular pH , the fraction is constant and may be calculated from the acid ionization constants and a material balance on Y^{4-} .

$$U = [H_4Y] + [H_3Y^-] + [H_2Y^{2-}] + [HY^{3-}] + [Y^{4-}] \quad (a)$$

$$K_1, \text{ or } 1.00 \times 10^{-2} = \frac{[H_3Y^-][H_3O^+]}{[H_4Y]} \quad (b)$$

$$K_2, \text{ or } 1.00 \times 10^{-3} = \frac{[H_2Y^{2-}][H_3O^+]}{[H_3Y^-]} \quad (c)$$

$$K_3, \text{ or } 1.00 \times 10^{-6} = \frac{[HY^{3-}][H_3O^+]}{[H_2Y^{2-}]} \quad (d)$$

$$K_4, \text{ or } 1.00 \times 10^{-10} = \frac{[Y^{4-}][H_3O^+]}{[HY^{3-}]} \quad (e)$$

Eqs. *a-e* may be used to find $[Y^{4-}]$.

$$U = [Y^{4-}] \left[1 + \frac{[H_3O^+]}{K_4} + \frac{[H_3O^+]^2}{K_4K_3} + \frac{[H_3O^+]^3}{K_4K_3K_2} + \frac{[H_3O^+]^4}{K_4K_3K_2K_1} \right] \quad (f)$$

At pH 5.00 $[Y^{4-}]$ may be calculated from U:

$$[Y^{4-}] = 9.0 \times 10^{-7} M \quad (g)^*$$

(a) After 50.20 ml of standard Na_2H_2Y are added, the total concentration of all forms of Y^{4-} in the mixture is $0.1000 \times 50.20/100.20$, or 0.05010 *M*. Likewise, the total M^{2+} is $0.1000 \times 50.00/100.20$, or 0.04990 *M*.

If x is defined to be $[M^{2+}]$, the concentration of uncomplexed M^{2+} , then the concentrations of the other species may be expressed in terms of x .

$$[MY^-] = 0.04990 - x \quad (h)$$

$$U, \text{ or uncomplexed } Y^{4-} = 0.05010 - (0.04990 - x) = 0.00020 + x \quad (i)$$

$$[Y^{4-}] = (0.00020 + x)(9.0 \times 10^{-7}) \quad (j)$$

Substituting Eqs. *h-j* into the stability-constant expression permits calculation of x :

$$\frac{[MY^-]}{[M^{2+}][Y^{4-}]} = K \quad (k)$$

$$\frac{(0.04990 - x)}{(x)(0.00020 + x)(9.0 \times 10^{-7})} = 1.00 \times 10^{14} \quad (l)$$

$$x, \text{ or } [M^{2+}] = 2.8 \times 10^{-6} M$$

$$pM = 5.56$$

(b) At the equivalence point, when 50.00 ml of each solution have been added, the total concentration of all forms of Y^{4-} is the same as the total concentration of all forms of M^{2+} , which is $0.1000 \times 50.00/100.00$, or 0.05000 *M*.

If z is defined as $[M^{2+}]$, the concentration of uncomplexed M^{2+} , then the concentrations of the other species may be expressed in terms of z .

$$[MY^-] = 0.05000 - z \quad (m)$$

$$U, \text{ or uncomplexed } Y^{4-} = 0.05000 - (0.05000 - z) = z \quad (n)$$

$$[Y^{4-}] = 9.0 \times 10^{-7} z \quad (o)$$

*This small fraction simply means that most of the Y^{4-} is in a protonated form other than Y^{4-} . Since pH 5 is close to the pK_3 of 6, the predominant forms are H_2Y^{2-} and HY^{3-} . Eq. *d* shows that $[H_2Y^{2-}]/[HY^{3-}] = 10$.

Substituting Eqs. *m-o* into the stability-constant expression permits calculation of *z*.

$$\frac{(0.0500 - z)}{z \times 9.0 \times 10^{-7} \times z} = 1.00 \times 10^{14}$$

$$z, \text{ or } [M^{2+}] = 2.36 \times 10^{-6} M$$

$$pM = 4.63$$

(*c*) When 49.70 ml of standard Na_2H_2Y are added, the total concentration of all forms of Y^{4-} is $0.1000 \times 49.70/99.70$, or $0.04985 M$, while the total concentration of all forms of M^{2+} is $0.1000 \times 50.00/99.70$, or $0.05015 M$.

If *w* is defined* as the concentration of all forms of uncomplexed Y^{4-} , then the concentrations of the other species may be expressed in terms of *w*.

$$[Y^{4-}] = 9.0 \times 10^{-7} w \quad (p)$$

$$[MY^{-}] = 0.04985 - w \quad (q)$$

$$[M^{2+}] = 0.05015 - (0.04985 - w) = 0.00030 + w \quad (r)$$

Substituting Eqs. *p-r* into the stability-constant expression permits the calculation of *w*.

$$\frac{(0.04985 - w)}{(0.00030 + w)(9.0 \times 10^{-7} w)} = 1.00 \times 10^{14}$$

$$w, \text{ or total uncomplexed } Y^{4-} = 1.8 \times 10^{-6} M$$

$$[M^{2+}] = 0.00030 + 1.8 \times 10^{-6} = 0.00030 M$$

$$pM = 3.52$$

From the answers, it is apparent that complexation of the added Y^{4-} is quantitative, and that the uncomplexed M^{2+} may be found as the stoichiometrical difference between the total M^{2+} and total Y^{4-} added. This is a faster way to do the problem than the above way. If the faster way is used, however, the answers obtained should be used to verify that complexation *is* quantitative for the particular case at hand. As a rule, for all points except those that are very near the equivalence point, the assumption of quantitative complexation turns out to be valid.

As the acidity is decreased, complexation is favored, and the inflection region becomes steeper. Curves for the titration at higher *pH* are also shown in Fig. 23.2. Conversely, raising the acidity hinders complexation and decreases the steepness of the inflection region. At a high enough acidity, complexation is nil and there is no inflection.

Figure 23.3 shows titration curves for several metal ions at various acidities. It may be seen that the alkaline earths must be titrated in alkaline solution, whereas Fe(III) is so strongly complexed that it may be titrated in highly acid solution. It may also be seen that Ni may be titrated accurately at *pH* 4 without interference by Ca or Mg.

*Before the equivalence point, it is the Y^{4-} that is in deficiency, and it is well to define its small concentration as the unknown. To define $[M^{2+}]$ as the unknown results in a complete loss of significant figures, which can be ascertained by the student.

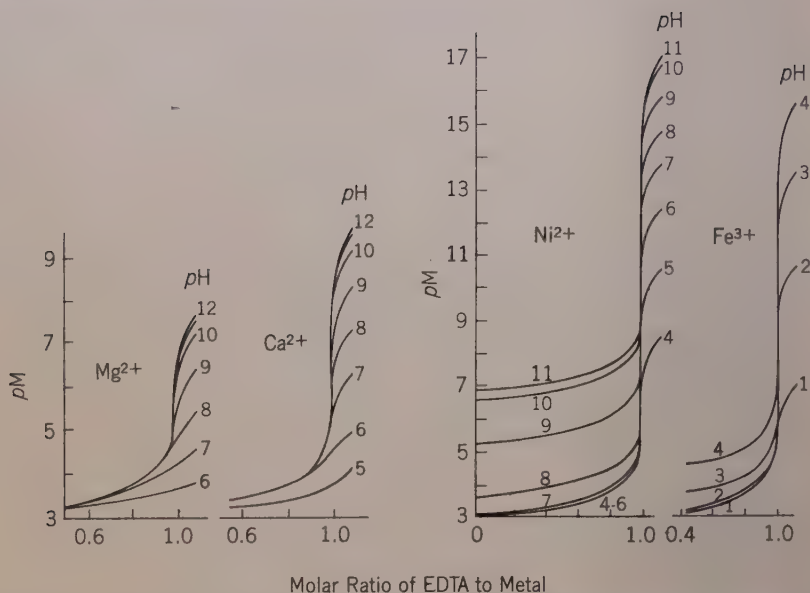


FIG. 23.3. Titration of Metal Salts with $\text{Na}_2\text{H}_2\text{Y}$ (Reprinted from G. Schwarzenbach, *Analyst*, 80, 713 [1955], Figs. 4 and 5, by permission of The Society for Analytical Chemistry.)

23C.3c. Equivalence point detection. The sharp rise in pM at the equivalence point may be detected in a variety of ways. A few of the more frequently encountered ways are described in this section. Many others are given in the literature.

Potentiometric titrations. The Hg-HgY^- electrode (**S4**). In theory, a pM titration curve may be followed potentiometrically with any electrode that involves the metal ion being titrated. In practice, there are very few metals that can be measured directly in this way. Amalgam electrodes of Cu, Zn, Cd, and Pb may be used to measure the concentration of the corresponding metal ions in solution, but the behavior is sluggish. Hg^{2+} is one of the few metal ions that can be determined accurately in this way, with a mercury metal electrode.

Fortunately, the Hg-Hg^{2+} electrode may be used indirectly to measure most metal ions that are titratable with EDTA. The potential-determining substance (Hg^{2+}) is in equilibrium with the metal ion (M^{m+}) to be determined. As pM changes in the region of the equivalence point, so does $p\text{Hg}$, and therefore so does the E of the Hg-Hg^{2+} electrode, as shown in the following paragraphs.

Suppose that a solution of M^{m+} is placed in the titration assembly of

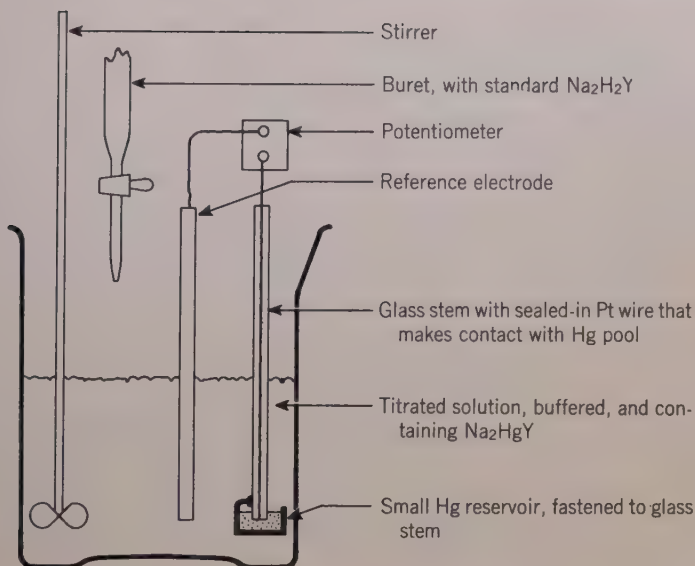
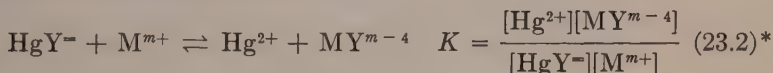
FIG. 23.4. The Hg-HgY^- Electrode in pM Titrations

Fig. 23.4, and that a small, definite concentration of Na_2HgY is added. According to the Nernst equation, the single-electrode potential of the Hg electrode is

$$E = E^\circ_{\text{Hg}} + \frac{0.0591}{2} \log [\text{Hg}^{2+}] \quad (23.1)$$

At any point in the titration, both HgY^- and MY^{m-4} are present, and the following equilibrium holds:



Equations 23.1 and 23.2 may be combined to eliminate $[\text{Hg}^{2+}]$, giving

$$E = E^\circ + 0.0286 \log \frac{K[\text{HgY}^-][\text{M}^{m+}]}{[\text{MY}^{m-4}]} \quad (23.3)$$

$$E = E^\circ + 0.0286 \log \frac{K[\text{HgY}^-]}{[\text{MY}^{m-4}]} - pM \quad (23.4)$$

* K is related to the stability constants of the HgY^- and MY^{m-4} complexes, K_{HgY} and K_{MY} , respectively:

$$K = \frac{[\text{Hg}^{2+}][\text{MY}^{m-4}]}{[\text{HgY}^-][\text{M}^{m+}]} \cdot \frac{[\text{Y}^{4-}]}{[\text{Y}^{4-}]} = \frac{K_{\text{MY}}}{K_{\text{HgY}}}$$

According to Eq. 23.4, if $[\text{HgY}^-]$ and $[\text{MY}^{m-4}]$ are kept constant, E varies linearly with pM , and a plot of E against volume of standard $\text{Na}_2\text{H}_2\text{Y}$ will give an S-shaped titration curve.

Although a fixed concentration of Na_2HgY is added initially, $[\text{HgY}^-]$ does not remain constant in the titration unless the stability of HgY^- is much greater than that of MY^{m-4} . Were the HgY^- complex not much more stable, Hg^{2+} would be displaced from its complex by M^{2+} , according to Eq. 23.2, and $[\text{HgY}^-]$ would change during the titration, destroying the linearity between E and pM . Fortunately, the HgY^- complex is more stable by orders of magnitude than almost all other MY^{m-4} complexes (Table 23.4), and the Hg-HgY^- electrode is applicable to almost all EDTA titrations. A list of the metals that may be titrated is given in Table 23.6.

$[\text{MY}^{m-4}]$ varies throughout the titration, but as the equivalence point is approached, it reaches its maximum concentration and does not change rapidly. In the vicinity of the equivalence point, therefore, changes in E are caused almost entirely by changes in pM .

The effect of pH is complicated. First, the pH must be high enough

TABLE 23.6
EDTA TITRATIONS WITH THE Hg-HgY^- ELECTRODE

$pH^{(1, 2)}$	Buffer Systems ⁽³⁾	Metal Ions That May Be Titrated
1.5-2.5	HNO_3 , or chloroacetic acid	Hg^{2+} , Bi^{3+} , Th(IV)
4.0-4.5	Acetate, or hexamethylene-tetramine	VO^{2+} , Mn^{2+} , Co^{2+} , Zn^{2+} , Cd^{2+} , Hg^{2+} , Pb^{2+} , RE^{3+} , * Zr(IV) , * Hf(IV) , * Th(IV) , * Al^{3+} , * Ga^{3+} , * In^{3+} , * Cr^{3+} , * Fe^{3+} , * Ni^{2+}
8.0-10.0	NH_3 , triethanolamine, ethanolamine	Mg^{2+} , Ca^{2+} , Sr^{2+} , Ba^{2+} , * Co^{2+} , * Ni^{2+} , * Cu^{2+} , * Zn^{2+} , * Cd^{2+} , * Pb^{2+} , * In^{3+} , * Hg^{2+} , * Ti^{3+} , * Bi^{3+} , * RE^{3+}

(1) Most metals determinable at a low pH are also determinable at a high pH , although sometimes a second complexer is needed to prevent the metal hydroxide from precipitating. Thus, In and Pb may be titrated directly at pH 8-10 in the presence of tartrate.

(2) Most metals listed at a high pH , but not at a low pH , do not interfere in titrations at a lower pH , which permits titration of mixtures. Thus, a solution containing Bi , Cd , and Ca may be analyzed for Bi by titration at pH 2, where neither Cd nor Ca interfere. After the Bi end point, the pH is adjusted to pH 4.5, where the Cd is titratable without interference from the Ca . Finally, the pH is adjusted to 8.5, and the Ca is titrated. Other combinations may be inferred from the table.

(3) Buffer must be present to prevent pH changes during titration. However, a large excess of buffer should be avoided, since this reduces the change in potential at the end point.

*The rate of reaction of these metals with EDTA is slow, which precludes direct titration. These metals may be determined indirectly, or by back titration.

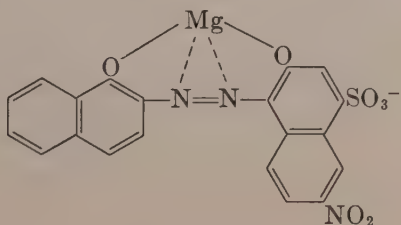
so that MY^{m-4} is not appreciably dissociated at the end point; otherwise the end point is not sharp. Second, acidic mixed complexes like MHY^{m-3} and $HgHY^-$ begin to form below pH 4, and at high pH (above 8), basic mixed complexes like $MOHY^{m-5}$ and $HgOHY^=$ begin to form. These cause deviation from linearity between E and pM , distorting the titration curve, and spreading out the inflection region. The titration becomes inaccurate below pH 2 or above pH 10.

While titrations may be performed in buffered solutions, substances that complex strongly with Hg^{2+} (such as Cl^- , Br^- , I^- , SCN^- , CN^- , and S^-) cannot be present.

It should be pointed out that the addition of Na_2HgY causes no error, since the Hg^{2+} and Y^{4-} are added in the form in which they exist at the equivalence point. Were the indicator added as $Hg(NO_3)_2$, however, a blank would be needed.

Metal indicators (B3). Metal indicators are organic dyes with acid-base indicator properties, that undergo a color change when a proton is transferred to or from the dye molecule. In addition, the dye molecule also contains a chelating group that includes the transferable proton, and that is joined to the conjugated system responsible for the color. In coordinating with a metal ion, the transferable proton is displaced at a pH below that at which the proton would be removed in the absence of the metal ion. In other words, coordination with a metal ion causes the indicator to transit to its basic form at a pH below the normal transition pH (K20).

A well-studied example is Eriochrome Black T (Erio T), an *o*, *o'*-dihydroxyazo dye whose properties are shown in Fig. 23.5. It has been shown that Erio T chelates with metals in 1:1 ratio over a wide range of conditions. The structure of the complex with Mg^* is believed to be



*Erio T satisfies 3 coordinate valencies on the Mg^{2+} . Since the two N's are identical, the $Mg-N$ coordinate bond probably resonates between the two N-atoms, as indicated by the dotted lines.

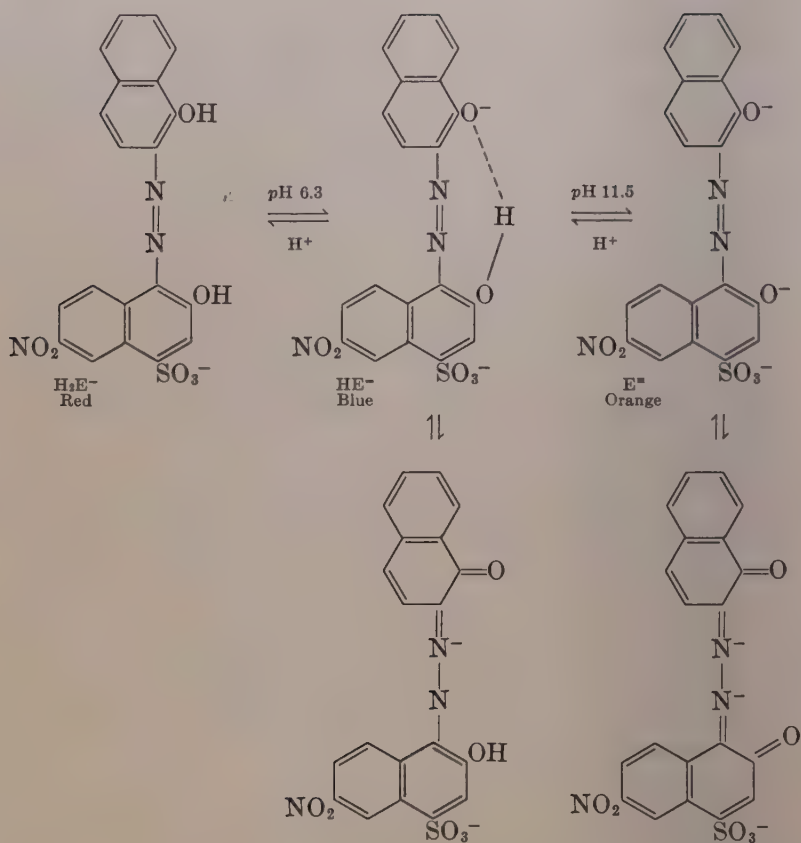
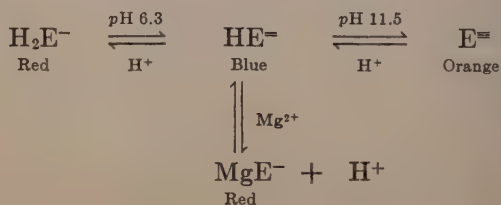


FIG. 23.5. Structures of Eriochrome Black T—Only two each of the many resonant forms of HE^- and $\text{E}^=$ are shown.

The equilibria involved in the color changes are



Very careful control of conditions is usually necessary for the proper functioning of a metal indicator. In particular, the pH must be correctly adjusted. Thus, Erio T must be used in the range pH 7–11, where the uncomplexed indicator is blue, so that the formation of the red Mg complex is readily perceptible. Outside the range pH 7–11, there is little contrast between the colors of the complexed and uncomplexed indicator.

Considerations other than color contrast further restrict the pH range at which Erio T can be used. If the pH is much lower than 10, the protonated form HE^- is too stable, and the Mg complex does not form until a considerable excess of Mg^{2+} is built up in the solution. If too basic, $Mg(OH)_2$ may form.

For use as an indicator in the titration of a metal with standard Na_2H_2Y , the stability constant of the metal-indicator complex must be about 10-fold smaller than the stability constant of the metal- Y^{4-} complex. If the indicator complex is too stable, the end point is premature; if not stable enough, the end point comes late. For example, Erio T is suitable for the titration of Mg^{2+} with standard Na_2H_2Y , but not for the direct titration of Ca^{2+} , which forms a less stable complex than Mg^{2+} with Erio T, and a more stable complex with Y^{4-} . However, Ca^{2+} may be determined indirectly using Erio T (p. 590).

The relatively high pH (7–11) at which Erio T must be used makes it unsuitable for titrations in strongly acid medium. However, a good selection of indicators is now available. Among these, xylenol orange (a sulfonphthalein dye) is very stable, shows a sharp color transition from red to yellow, and can be used in strongly acid medium. For example, $Zr(IV)$ can be titrated with EDTA in 1 M HNO_3 , which is an acidity sufficiently high to prevent interference by most other metals. With pyrocatechol violet, over 30 metals may be titrated with EDTA in the range pH 0.5–9.5 (S32).

Photometric titrations (H6). A few metals (Cu , Ni , Fe) form colored complexes with EDTA and may be titrated photometrically (p. 541). A plot of absorbance against volume of titrant gives a broken type of titration curve. A solution of the metal ion may be titrated with standard Na_2H_2Y or vice versa.

Many variations permit the photometric titration of colorless metal ions that form colorless EDTA complexes: (a) Pb^{2+} and Bi^{3+} may be titrated in the ultraviolet, where the absorbances of complexed and uncomplexed EDTA differ. (b) Bi^{3+} can be titrated if an unmeasured amount of Cu^{2+} (which forms a much weaker EDTA complex) is added to the sample. The absorbance remains low until the Bi^{3+} is complexed, after which it increases as the Cu^{2+} -EDTA complex is formed. (c) A

metal that forms a colorless complex may also be determined by back titration, after adding a measured excess of EDTA, the excess being titrated with a standard solution of a metal that forms a colored complex with EDTA. (d) Fe^{3+} may be determined by adding an unmeasured excess of salicylic acid, which forms a colored Fe^{3+} -salicylate complex. The solution of the colored complex is then titrated with standard EDTA.

With some metal indicators, the color transitions are not easily perceptible to the eye, either because the two limiting colors are not complementary, or because the change is too gradual. In such cases, spectrophotometric observation of the end point may improve accuracy, the spectrophotometer being set at a wavelength for which there is a maximum difference in absorbance between the free indicator and its metal complex. The titration curve has a double break, as shown in Fig. 23.6 for the titration of Mg^{2+} with EDTA, a trace of Eriochrome Black T being used as an indicator. The absorbance due to the Mg^{2+} -Erio indicator complex remains constant throughout most of the titration, while the free Mg^{2+} is being titrated. After all of the free Mg^{2+} is complexed, the color changes abruptly as the Mg^{2+} is displaced from the trace of Mg^{2+} -Erio complex by further addition of EDTA. After the Mg^{2+} in the Mg^{2+} -Erio complex has been titrated, further addition of EDTA produces no further change in absorbance. The curve appears S-shaped because only a small fraction of the original Mg^{2+} is bound as the Mg^{2+} -Erio complex. The correct equivalence point is not at the inflection point, but rather when all of the Mg^{2+} has been titrated, including that originally bound as the Mg^{2+} -Erio complex.

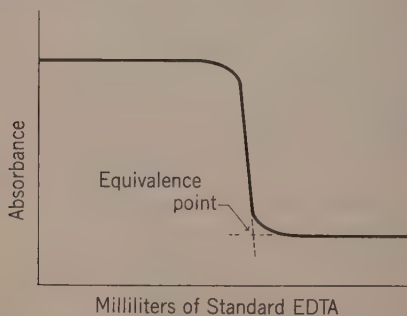


FIG. 23.6. Photometric Titration of Mg with EDTA, Erio T as Indicator ($\kappa 1$)—Conditions: 20 ml of 0.05 M MgCl_2 in $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer (pH 10), titrated with 0.05 M EDTA. End-point volume, 150 ml. Wavelength, 546 m μ , where free Erio T has a lower absorbance than the Mg^{2+} -Erio complex.

23C.3d. Titration techniques. Figure 23.7 lists the elements that may be determined with EDTA. While many elements are directly titratable with standard EDTA, some must be titrated indirectly.

1A	2A	3A	4A	5A	6A	7A	8	1B	2B	3B	4B	5B	6B	7B		
Li	Be									B	C	N	O	F		
Na	Mg									Al	Si	P	S	Cl		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I
Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At
Fr	Ra	†														
Lanthanides	La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinides	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Ct	Md	No	103	

By direct or back titration

Indirectly

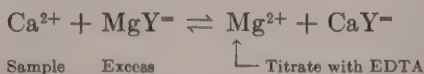
No methods reported before 1962

FIG. 23.7. Elements Titratable with EDTA and Visual Indicators (Updated version of Fig. 1 from H. Flaschka, A. J. Barnard, Jr., and W. C. Broad, *Chemist-Analyst*, 46, 107 [1957], kindly supplied by A. J. Barnard, Jr., editor, *Chemist-Analyst*.)

Some metals might precipitate at the pH required for titration. In such cases, an excess of standard Na_2H_2Y may be added, the pH adjusted, and the excess EDTA then back-titrated with a standard metal ion solution, like $MgCl_2$ or $ZnCl_2$. The sought-for metal ion is complexed by the excess EDTA and does not precipitate, even at a pH sufficiently high to cause precipitation of the uncomplexed metal ion. With this technique, even precipitates like $PbSO_4$ and CaC_2O_4 can be titrated. There are some metal ions (i.e., Al^{3+} , Ni^{2+}) that react too slowly with EDTA for direct titration, but that can be determined by *back titration*.

There is a variety of *indirect methods*, in which the standard EDTA does not react with the sought-for substance, but with another substance that is stoichiometrically related to the sought-for one. For example, PO_4^{3-} may be determined by precipitation as $MgNH_4PO_4$, followed by titration of the Mg^{2+} with standard EDTA. Ca^{2+} cannot be titrated directly using Erio T indicator, because it does not form a strong enough

complex with the indicator. However, an excess of a solution containing the 1:1 MgY^- complex may be added to the Ca^{2+} sample. The Ca^{2+} forms a tighter EDTA complex and displaces an equivalent amount of Mg^{2+} , which is then titrated with the standard EDTA.



23D. OTHER CHELATING TITRANTS

It has been pointed out that selectivity is obtainable in complexation titrations by: (1) adjustment of the $p\text{H}$, and (2) use of masking reactions (see examples on pp. 569–70). The ability to choose among a number of chelating titrants adds a third dimension to the selectivity obtainable in complexation titrations. Tables 23.4 and 23.5 give properties of a few chelating agents that are available in purities sufficient for titrations.

Inspection of Table 23.4 reveals that EGTA is more useful than other titrants for the determination of Ca^{2+} in the presence of Mg^{2+} . Also, the polyamine type of titrant is particularly useful for determination of transition metals in the presence of alkaline earths, rare earths, Al^{3+} , and heavy metals (like Pb^{2+}).

EXPERIMENT 23.1. DETERMINATION OF Ca , Mg , AND Fe IN LIMESTONE BY EDTA TITRATION

INTRODUCTION

The composition of limestones is given on page 481. In the following procedure (R6), Ca , Mg , and Fe are determined on separate aliquots of a master sample solution. The Ca and Mg aliquots are titrated directly with standard EDTA. The Fe aliquot is treated with excess standard EDTA, the excess being back-titrated with standard $\text{Bi}(\text{NO}_3)_3$.

PROCEDURE

1. Preparation of standard solutions.

1a. 0.02 M EDTA. Weigh 3.722 g of reagent-grade $\text{Na}_2\text{H}_2\text{Y} \cdot 2\text{H}_2\text{O}$ into a 250-ml beaker, transfer to a 500-ml volumetric flask, dissolve, and make up to volume. (Notes 1–3.)

1b. 0.02 M $\text{Bi}(\text{NO}_3)_3$. Dissolve 2.5 g of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in 6 ml conc. HNO_3 plus 20 ml of distilled water. (Note 4.) Make up to about 250 ml, mix well, and store in a glass-stoppered bottle. To standardize, pipet a 10-ml aliquot into a 250-ml Erlenmeyer flask, dilute to about

100 ml with distilled water, add 4 drops of xylenol orange, and titrate with the 0.02 M $\text{Na}_2\text{H}_2\text{Y}$. The end point is the disappearance of the last tinge of pink, after which the indicator assumes its uncomplexed pure yellow form. (Notes 5, 6.) Calculate the milliliters of 0.02 M $\text{Na}_2\text{H}_2\text{Y}$ that are equivalent to 1 ml $\text{Bi}(\text{NO}_3)_3$.

2. *Sample preparation.* Weigh a 0.500-g portion of the dried limestone sample (step 3a, p. 484) into a 250-ml Erlenmeyer flask, and add 3 ml of distilled water. Add 3 ml conc. HCl with a dropper, exercising care to prevent loss by effervescence. Heat just below boiling for 2–3 minutes. (Note 7.) Then add 20 ml of water and 5 drops of saturated bromine water, and boil gently for 3–4 minutes to expel excess bromine. (Note 8.) Cool, transfer quantitatively to a 100-ml volumetric flask, and make up to volume with distilled water. (Notes 9, 10.) This solution is called the “master sample solution.”

3. *Determination of Ca.* Pipet a 20-ml aliquot (Note 11) of the master sample solution into a 250-ml Erlenmeyer flask, and add about 100 ml of water. Add 1 g ascorbic acid, stir, and permit to stand for about 3 minutes. (Note 19.) Add 20 drops of 50% NaOH and 0.1 g of NaCN . (CAUTION! Note 12.) Warm to about 50°C , and swirl occasionally for 3–4 minutes. (Notes 13–15.) Cool, add 1 drop of Calcon indicator, and titrate with the 0.02 M $\text{Na}_2\text{H}_2\text{Y}$. The end point is the disappearance of the last tinge of pink, after which the indicator assumes its uncomplexed blue color. (Notes 6, 16.) The end point should persist for at least 20 seconds, the solution being swirled constantly. (Note 17.) Calculate and report the Ca content of the sample as % CaO .

4. *Determination of Mg.* Pipet a 20-ml aliquot (Note 18) of the master sample solution into a 250-ml Erlenmeyer flask, add 1 g ascorbic acid, stir, and allow to stand for 3 minutes. (Note 19.) Add 5 drops of 50% NaOH and 0.1 g KCN . (CAUTION! Note 12.) Warm to 50°C , and stir occasionally for 2–3 minutes. (Notes 13–15.) Cool, add 1 ml of pH 10 buffer, 2 drops of Erio T, and titrate with the 0.02 M $\text{Na}_2\text{H}_2\text{Y}$. The end point is the disappearance of the last tinge of red (i.e., purple), after which the indicator assumes its uncomplexed blue color. (Note 6.) Calculate and report the Mg content of the sample as % MgO . (Note 20.)

5. *Determination of Fe.* Pipet a 50-ml aliquot of the master sample solution into a 250-ml Erlenmeyer flask, and add about 50 ml of water. Add a carefully measured excess of the 0.02 M $\text{Na}_2\text{H}_2\text{Y}$. (Notes 21, 22.) Let stand with occasional stirring for 3 minutes. Add 2 drops of xylenol orange (Note 23) indicator, and back-titrate with standard $\text{Bi}(\text{NO}_3)_3$. The end point is the first permanent tinge of pink that is perceptible against the pure yellow color of the uncomplexed indicator. Calculate and report the Fe content as % Fe_2O_3 .

NOTES

(1) The dihydrate is a good primary standard, being stable over a wide range of conditions. When taken from the reagent bottle, its composition is almost always within a few tenths of a per cent of the theoretical. For accurate work, it is desirable to dry the material for an hour around 50°C before weighing out. The reactions with Ca, Mg, and Fe are stoichiometrical, blanks are nil, and further standardization is not required.

(2) The dissolution of the salt is slow, and may take the better part of a half hour, with occasional swirling.

(3) $\text{Na}_2\text{H}_2\text{Y}$ solutions undergo no changes in titer during storage for a few weeks in borosilicate glass bottles. For longer storage, or for more accurate work, storage in plastic bottles is preferred.

(4) Do not warm to hasten solution, lest hydrolysis and precipitation of Bi(III) occur.

(5) Run a blank with 10 ml of water instead of $\text{Bi}(\text{NO}_3)_3$ solution. A blank below 0.02 ml may be ignored. A larger blank indicates impurities in the water or reagents, in which case the instructor should be consulted.

(6) The color transitions of metal indicators are sharp, but delicate. Observe the changes in a clean flask placed on white paper, and with good illumination.

(7) This experiment is performed at the 1% error level, and does not require the rigorous extraction that a more accurate determination at the 0.1% error level does (p. 481).

(8) Bromine oxidizes any Fe(II) to Fe(III).

(9) There is not enough master sample solution to perform replicate titrations on all components. If duplicate determinations are desired, another master sample solution should be prepared, rather than a larger, single master sample solution, so that the extraction step is checked as well as the titrations.

(10) The disposition of any residue (mostly silica) is immaterial. It need not be transferred quantitatively. Neither need it be filtered off, since it does not interfere in the titrations.

(11) The aliquot size is such that about 9 ml of 0.02 M $\text{Na}_2\text{H}_2\text{Y}$ is required for each 10% of CaO in the limestone. If necessary, the instructor should recommend a more appropriate aliquot size for the samples at hand.

(12) NaCN is an extremely dangerous systemic poison. An oral dose of 200 mg is fatal to humans in most cases, and toxic effects are noticeable for much smaller amounts. It can also be absorbed through the skin, particularly through cuts or abrasions. Handle NaCN carefully and neatly. Any spillage should be cleaned up immediately. Hands should be washed carefully after working with NaCN. It should never be put in acid solutions, except in a good hood, for it is converted to HCN, a very toxic gas. For disposal, at the end of each titration, add 1 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ to the titration flask, to convert CN^- to harmless $\text{Fe}(\text{CN})_6^{4-}$, and flush into the drain with generous amounts of water.

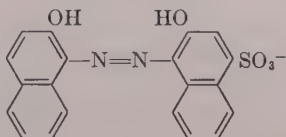
(13) The NaCN prevents interference of elements like Cu, Ni, and Fe, by complexing them so strongly that they do not react with EDTA.

(14) Even if present in stoichiometrically insignificant amounts, elements like Ni and Cu can interfere by "blocking" the indicator. Just a trace of Ni(II) can complex with the indicator to give the pink color of the Ni-Calcon complex, which dissociates so slowly that the pink color persists even after the Ca end point is passed and after the solution contains excess EDTA. The NaCN binds Ni and Cu so that they cannot block the indicator. Erio T is blocked in the same way.

(15) The Cu, Ni, and Fe may precipitate as hydroxides upon addition of NaOH. The heating and stirring aid conversion of the hydroxides to the soluble complex

cyanides. The Mg is precipitated as $\text{Mg}(\text{OH})_2$. The carbonate that is invariably present in the added NaOH causes at least partial precipitation of the Ca.

(16) Calcon (Eriochrome Blue Black R) is an *o*, *o'*-dihydroxyazo dye, closely related to Erio T:



It is blue in the range pH 8–12, and pink in strongly basic solutions.

(17) By working around pH 12, Ca^{2+} can be titrated in the presence of Mg^{2+} , for the Mg^{2+} is precipitated as the hydroxide and does not react with the $\text{Na}_2\text{H}_2\text{Y}$. Because some of the Ca is precipitated as CaCO_3 , the end point is sluggish. The solution should be swirled well in the vicinity of the end point, to aid the dissolution of CaCO_3 , and to ensure that the end point is permanent. To detect the end point, the EDTA should be added in dropwise increments (no less) near the end point. A point in the titration will be reached at which a drop of the EDTA will cause the solution to turn blue, but the pink will fade back within 20 seconds. At this point, it is desirable to let the solution stand with occasional swirling for 5 minutes before completing the titration, to permit complete dissolution of the CaCO_3 .

(18) The aliquot size is such that about 9 ml of 0.02 *M* $\text{Na}_2\text{H}_2\text{Y}$ is required for each 10% of CaO in the sample, and about 12 ml for each 10% of MgO. If necessary, the instructor should recommend a more appropriate aliquot size for the samples at hand.

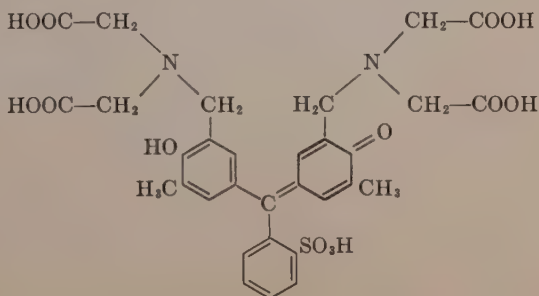
(19) The ascorbic acid reduces any oxygen in solution. Erio dyes are subject to air-oxidation, the oxidation being catalyzed by metal ions such as Mn(II).

(20) Both Ca^{2+} and Mg^{2+} are titrated at pH 10. The volume of 0.02 *M* $\text{Na}_2\text{H}_2\text{Y}$ corresponding to the Mg^{2+} in the master sample aliquot is the difference between the volumes of $\text{Na}_2\text{H}_2\text{Y}$ used in this step and in step 3.

(21) The instructor should give the approximate Fe content of the sample. Add about 1.7 ml of 0.02 *M* $\text{Na}_2\text{H}_2\text{Y}$ for each 1% of Fe_2O_3 in the sample, plus an excess of about 1 ml, measuring the total volume to the nearest 0.01 ml.

(22) Fe(III) is complexed too slowly by EDTA to permit direct titration, so a back titration technique is used.

(23) Xylenol orange is a sulfonphthalein dye whose acid-base properties have been thoroughly studied (R2).



It may be used as a metal indicator in strongly acid solution. So, advantage may be taken of the great stability of the FeY^- complex to perform the titration at

an acidity high enough to preclude interference by the other metals that are likely to be present in limestone.

QUESTIONS

Section 23A

1. In the aluminum oxinate complex on page 569, which are the electron donor and acceptor atoms?

2. Write the structure of the 1:1 complex between Zn^{2+} and triethylenetetramine. Repeat for triaminotriethylamine.

3. Give an example of a tridentate complexer, and write the structures of two of its complexes with Cu^{2+} .

4. Write the structures of the complexes that might be formed between Cu^{2+} and phthalic acid: (a) at a high ratio of Cu^{2+} to phthalic acid, (b) at a low ratio of Cu^{2+} to phthalic acid.

5. For the complex between Ni^{2+} and ethylenediamine, $\log K_1$ and $\log K_2$ are 7.60 and 6.48, respectively. For the N, N'-dimethylethylenediamine complex, $\log K_1$ and $\log K_2$ are 6.65 and 3.85, respectively. Explain why the methyl-substituted ethylenediamine forms less stable complexes.

Section 23B

1. Ag^+ is not reduced by Fe^{2+} in aqueous solution. In the presence of EDTA, however, Ag^+ is reduced by Fe^{2+} . Explain.

2. When KI is added to an FeCl_3 solution at pH 2–3, iodine is formed. When $\text{Na}_2\text{H}_2\text{Y}$ is added, the iodine color disappears. Explain.

3. Explain why Fe(II) is oxidized by air much more easily in the presence of $\text{Na}_2\text{H}_2\text{Y}$ than in its absence.

4. Write the equation for the dissolution of aluminum 8-hydroxyquinolate in excess HCl to form 8-hydroxyquinolinium ion.

Section 23C

1. Explain why a solution of HgCl_2 cannot be accurately titrated with standard KSCN. However, HgCl_2 in unbuffered solution can be directly titrated with standard KCN, using a pH meter to establish the equivalence point. Explain the reactions that are involved in this method (M22).

2. The titration of halides with standard $\text{Hg}(\text{NO}_3)_2$ may be followed potentiometrically by adding a few drops of 0.03 M $\text{K}_3\text{Fe}(\text{CN})_6$ containing a few per cent of $\text{K}_4\text{Fe}(\text{CN})_6$ to the titration mixture. Given that $\text{Hg}_2\text{Fe}(\text{CN})_6$ is very insoluble, explain the indicator action, and plot a typical titration curve.

3. Outline a procedure whereby Ni(II) may be determined indirectly by the Liebig method.

4. In Fig. 23.1 (p. 575), reconcile the diethylenetriamine titration curve with the statement that Zn(II) has a coordination number of 4.

5. Each of the four ionizable protons occupy identical positions in the EDTA molecule. Why, then, do the stepwise acid ionization constants decrease?

6. Outline a method for determining the stability constant for ZnY^- , assuming that the four ionization constants for H_4Y are known.

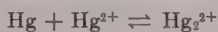
7. List and discuss the factors that determine the steepness of the inflection region of a titration curve like that in Fig. 23.2 (p. 579), for the titration of a metal ion with EDTA.

8. In the curves of Fig. 23.3 (p. 582): (a) Explain why the starting $p\text{Fe}$ rises as the pH rises. (b) Explain why the starting $p\text{Ni}$ rises as the pH rises, given that the titrations are performed in $\text{NH}_3\text{--NH}_4\text{Cl}$ buffers. (c) Explain why, for any particular

metal ion, the steepness of the curve in the inflection region does not increase without limit as the pH increases.

9. How would the Cu^{2+} titration curve at pH 8 compare with that for Ni^{2+} in Fig. 23.3, if the titration is performed in NH_3-NH_4Cl buffer? (Consider the relative stabilities of the NH_3 and EDTA complexes of Cu^{2+} and Ni^{2+} .)

10. If metallic Hg is contacted with a solution containing Hg^{2+} , show that the following reaction takes place, according to the table of standard potentials:



Explain why this reaction causes no difficulty when the Hg-HgY⁻ electrode is used for EDTA titrations.

11. Assuming that none is available, devise a procedure for the preparation of 0.01 M Na_2HgY solution.

12. The Hg-HgY⁻ electrode is called an electrode of the "second kind," because its potential is affected by, and may be used for measurement of, the concentration of any other metal ion that reacts with Y^{4-} . Show that the Ag-AgCl electrode is an electrode of the "second kind."

13. Draw an S-shaped curve to represent the titration of a particular metal ion with the Hg-HgY⁻ electrode under a particular set of conditions. On the same plot, show the effect on the titration if: (a) a higher concentration of Na_2HgY is used; (b) a pH higher by about $\frac{1}{2}$ –1 pH unit is used, but not so high that interfering reactions occur; (c) a pH sufficiently high to cause formation of $HgOHY^=$ is used; (d) a small amount of KSCN is added to the sample.

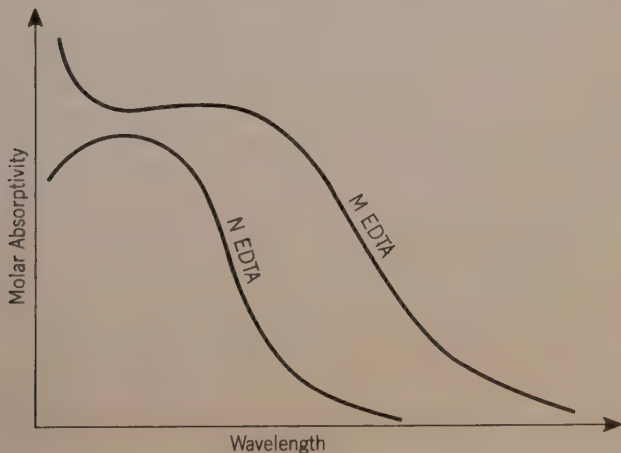
14. At about what pH would the protonation of $-SO_3^-$ occur on Erio T? Would an absorbance change accompany this protonation? What is the function of the $-SO_3^-$ group on Erio T?

15. Write the structures of some of the other resonant forms of HE^- and $E^=$ for Erio T.

16. Outline a procedure for finding the composition of the complex between Mg^{2+} and Erio T.

17. Draw a titration curve for the conditions of Fig. 23.6 (p. 588), except that the wavelength is 630 $m\mu$, where Erio T has a higher molar absorptivity than the Mg^{2+} -Erio T complex.

18. Two metal ions, M and N, form stable EDTA complexes, the stability of the M-EDTA complex being much greater than that of the N-EDTA complex. The



molar absorptivities of the complexes are given in the accompanying figure. Devise a procedure by which M and N might be determined in a single sample.

19. The titration of an Fe(III) sample with standard $\text{Na}_2\text{H}_2\text{Y}$ may be followed potentiometrically by adding a trace of Fe(II) as an indicator. Explain the nature of the indicator action, and draw a typical titration curve. Why would it be necessary to exclude air during the titration?

20. Before metal indicators became available, EDTA titrations were performed with standard base, as follows: (a) Neutralize the sample solution of the metal ion to be titrated so that it contains no excess of either acid or base. (b) Add an unmeasured excess of $\text{Na}_2\text{H}_2\text{Y}$. (c) Titrate the liberated acid with standard base to pH 5–6, which is the pH imparted by the excess $\text{Na}_2\text{H}_2\text{Y}$. Explain the limitations of this procedure.

21. Suppose that a standard $\text{Na}_2\text{H}_2\text{Y}$ solution has extracted Ca^{2+} from the storage bottle, and suppose also that the solution is restandardized by titration against a standard CaCl_2 solution at pH 10. Which value (the original, or restandardized) would be the better to use for the titration of Zn^{2+} with xylene orange at pH 6?

22. Devise an indirect EDTA titration for Ag(I), which does not complex with EDTA.

23. Devise EDTA titration procedures for the determination of each component in the following mixtures, without prior separation: (a) Al^{3+} , Fe^{3+} ; (b) Pb^{2+} , Zn^{2+} , Fe^{3+} ; (c) Ca^{2+} , Bi^{3+} , Pb^{2+} ; (d) Zn^{2+} , Fe^{3+} , Cu^{2+} , Ca^{2+} .

Section 23D

1. Devise procedures with complexing titrants for the determination of each component in the following mixtures, without prior separations: (a) Fe^{3+} , Ca^{2+} , Zn^{2+} , Cu^{2+} ; (b) Cu^{2+} , Zn^{2+} , Bi^{3+} , Pb^{2+} , Mg^{2+} .

PROBLEMS

Section 23A

1. Calculate the solubility of AgI in 0.10 M NH_3 . *Ans.* 3.9×10^{-6} M.
 2. What is the solubility of $\text{Hg}(\text{OH})_2$ in 0.50 M NaCl buffered at pH 11.00?
 3. A solution contains 0.00010 M AgNO_3 and 0.00030 M NH_3 . HCl is added to this solution. (a) Calculate the total molar concentration of all Ag^+ -bearing species for the following added concentrations of HCl: 0.00010, 0.00020, 0.00030, 0.00040, 0.0010, 0.010 M. (b) At which of the preceding HCl concentrations is the total concentration of Ag^+ -bearing species in solution a minimum?

Ans. (a) 1.8×10^{-5} M (at 0.00010 M HCl); (b) 0.0010 M HCl.

4. Calculate the concentrations of Fe^{3+} , FeCl_2^+ , FeCl_2^+ , and FeCl_3 as NH_4Cl is added to 0.0010 M $\text{Fe}(\text{ClO}_4)_3$ and plot these concentrations on a single graph as a function of added NH_4Cl (in moles per liter). Assume a pH sufficiently low so that hydroxy and polymeric species may be neglected.

5. For the assumption of Prob. 4 to hold, and so that $[\text{FeOH}^{2+}]/[\text{Fe}^{3+}]$ is always less than 0.01, at what pH would the solution have to be buffered? (See Appendix V.)

Ans. At pH 0 or less.

6. Where E represents ethylenediamine, calculate $[\text{Cu}^{2+}]$, $[\text{CuE}^{2+}]$, and $[\text{CuE}_2^{2+}]$ in a solution containing 0.0010 M $\text{Cu}(\text{ClO}_4)_2$, for several total concentrations of E in the range 0 to 0.0025 M. Assume the pH to be so high that only a negligible proportion of the uncomplexed E is in the acid form. Graph the results.

7. Rework Prob. 6, if the solution is buffered at pH (a) 8.00, (b) 5.00.

Ans. (a) At pH 8, for a total E concentration of 0.0025 M, $[\text{Cu}^{2+}] = 6.4 \times 10^{-12}$ M, $[\text{CuE}^{2+}] = 4.2 \times 10^{-7}$ M, and $[\text{CuE}_2^{2+}] = 0.0010$ M.

8. In Ex. 2 (p. 563), express the percentages of M^{2+} that are in the complexed form at pH 5 and pH 2. Also calculate the percentages of M^{2+} that are complexed at pH 3, 4, and 6, and plot. Discuss the shape of the curve.

9. A solution contains 0.010 M HX ($K_a = 1.0 \times 10^{-5}$), and a trace of the salt MCl (completely ionized). When the solution is buffered at pH 4.00, a potentiometric measurement shows 1.25% of the $M(I)$ to be in the uncomplexed form. At pH 5.00, 0.23% of the $M(I)$ is uncomplexed. Assume that only a single complex MX_n^{1-n} is formed. Calculate n and the stability constant for the complex.

Ans. $n = 1$; $K = 9 \times 10^4$.

Section 23B

1. A 5.76-g portion of an $MgCl_2$ solution gives a magnesium oxinate (8-hydroxyquinolate) precipitate weighing 0.916 g. Calculate the percentages of Mg and of $MgCl_2$ in the original solution.

Ans. 1.236% Mg , 4.84% $MgCl_2$.

2. A solution contains 0.0020 M $CdCl_2$ and 0.0030 M anthranilic acid (*o*-aminobenzoic acid). When base is slowly added to the solution, the first permanent trace of cadmium anthranilate appears at pH 5.26. Calculate the solubility product of cadmium anthranilate. (pK_a for anthranilic acid is 5.17.)

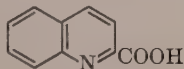
3. A 0.0010 M $CuCl_2$ solution is buffered at pH 4.00. Calculate the % Cu left in solution if 0.0050 moles of anthranilic acid (*o*-aminobenzoic acid) are added per liter of solution. For anthranilic acid, pK_a is 5.17. For copper anthranilate, pK_s is 13.22.

Ans. 0.17%.

4. If the solution in Prob. 3 also contains 0.0010 M $MnCl_2$, will any manganous anthranilate ($K_s = 5.3 \times 10^{-7}$) precipitate? How high may the pH be made before manganous anthranilate begins to precipitate?

5. Water is added to 1.00 mmole of $NiCl_2$ and 4.00 mmoles of quinaldinic acid ($pK_a = 4.90$), to give 50.0 ml of solution. What percentage of the Ni will be precipitated? (For nickel quinaldinate, pK_s is 10.10.)

Ans. 3.8%.



Quinaldinic acid

6. A solution contains $CdCl_2$ and $CuCl_2$, each at 0.0010 M . Devise conditions that will permit a separation of the two metals by precipitation with quinaldinic acid. The quinaldinates of copper and cadmium have pK_s values of 16.80 and 12.30, respectively. For quinaldinic acid, pK_a is 4.90. For the selected conditions, calculate the percentage of $Cu(II)$ precipitated.

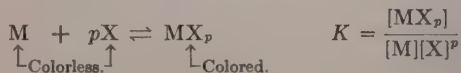
7. This problem deals with a rather specialized application of chelating agents, but a very important one—that of *metal buffers*. Many chemical reactions, some of biological significance, are catalyzed by low concentrations of metal ions. In the study of such reactions, it is often desirable to buffer the system at a low concentration of the metal ion. (a) With chemical equations, show that a system containing 0.10 M Na_2ZnY and 0.10 M Na_2H_2Y is buffered with respect to the zinc ion concentration, and that the value of $[Zn^{2+}]$ is pH-dependent (M7). (b) Calculate $[Zn^{2+}]$ if the solution is buffered at pH 8.00. (c) If a reaction occurs in the system to use up 0.01 mole of $Zn(II)$ per liter, so that the composition becomes 0.09 M Na_2ZnY and 0.11 M Na_2H_2Y , calculate the percentage change in $[Zn^{2+}]$. Assume that the system remains adequately buffered at pH 8.00. *Ans.* (b) $3 \times 10^{-15} M$; (c) 18% decrease.

8. A solution contains $1.00 \times 10^{-5} M$ each of MCl_3 and NCl_2 , which form colored complexes with the complexing agent HX ($K_a = 1.00 \times 10^{-6}$).



What pH range may be chosen for a spectrophotometric determination of $M(III)$, so that over 99% of the $M(III)$ is complexed, while less than 1% of the $N(II)$ is complexed? In the determination, the total HX in the system is 0.0100 M .

9. A metal ion (M) forms a complex:

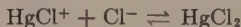


A series of mixtures of M and X is made up. The ratio of total M concentration to the total X concentration varies from one mixture to another, but the sum of the two total concentrations is the same ($C M$) in all mixtures. If x is the total X concentration, then $C - x$ is the total M concentration. If the absorbance of each mixture is measured and plotted against x , show that the maximum absorbance comes when $x/(C - x) = p$. This procedure is used to determine the composition of complex ions, and is called the *method of continuous variations* (M7).

Section 23C

1. A solution is prepared by mixing 100 ml of 0.00100 M $NaCl$, 100 ml of 0.300 M NH_3 , and 100 ml of 0.100 M $AgNO_3$. Will $AgCl$ precipitate? *Ans.* No.

2. A solution containing 0.1000 M KCl is to be titrated with standard 0.0500 M $Hg(NO_3)_2$ to the $HgCl_2$ equivalence point. (a) Describe an electrode system suitable for performing the titration potentiometrically. (b) Give a schematic of apparatus for making the measurements. (c) Calculate $[Hg^{2+}]$ and the single-electrode potential at the equivalence point, assuming that the only important equilibrium at the equivalence point is



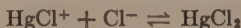
(d) Sketch a typical titration curve. (e) Calculate the concentrations of $HgCl_3^-$ and $HgCl_4^{2-}$ at the equivalence point. Describe roughly the error that is caused in the answer of part c by the neglect of these concentrations.

Ans. (c) $1.7 \times 10^{-7} M$, 0.655 v.

3. What is the maximum pH at which the titration of Prob. 2 could be performed, in order that no $Hg(OH)_2$ precipitates at the equivalence point? Neglect formation of $HgOH^+$. *Ans.* 4.78.

4. Calculate the concentrations of the Hg^{2+} -bearing species in a solution containing 0.0333 M KCl and 0.0333 M $Hg(NO_3)_2$, which corresponds to the half-way point and the formation of $HgCl^+$ in the titration of Prob. 2. Does the curve undergo a sharp inflection at this point?

5. For the titration of 0.1000 M KCl with standard 0.0500 M $Hg(NO_3)_2$, give the change in pHg or pCl in passing from 0.10% before the equivalence point to 0.10% after. Assume that the only important equilibrium is



Discuss the assumption.

Ans. 0.25 pHg unit.

6. For iodide to be a good indicator in the Liebig method for cyanide: (a) AgI must be insoluble in NH_3 solution. Show this to be the case, assuming that the total

NH_3 concentration is 0.50 M . (b) Also, AgI must be soluble in KCN solution. Show this to be the case, by finding the $[\text{I}^-]$ that could exist without precipitation of AgI in a solution containing 0.0500 M $\text{KAg}(\text{CN})_2$ and 0.000010 M KCN , which represents a point in the titration of 0.2000 M KCN with standard 0.1000 M AgNO_3 that is slightly past the equivalence point.

7. Calculate the end-point error in the Liebig titration of 0.0100 M KCN with 0.0100 M AgNO_3 . Assume that $[\text{NH}_3] = 0.100 M$ and that $[\text{I}^-] = 0.0100 M$ around the equivalence and end points. Assume that 1.0×10^{-6} moles of AgI per liter must be precipitated in order to see the end point. *Ans.* -0.32% (excess KCN).

8. In the indirect titration of Ni(II) by the Liebig method, Ag^+ and Ni^{2+} react with CN^- stoichiometrically to form $\text{Ag}(\text{CN})_2^-$ and $\text{Ni}(\text{CN})_4^{2-}$. A 25.00-ml portion of standard KCN is added to 10.00 ml of a $\text{Ni}(\text{NO}_3)_2$ sample solution, and the excess KCN requires 5.51 ml of 0.1013 M AgNO_3 for titration. A 25.00-ml portion of the standard KCN requires 25.62 ml of the 0.1013 M AgNO_3 for titration. What is the molarity of the $\text{Ni}(\text{NO}_3)_2$ solution?

9. Under the conditions of Fig. 23.2 (p. 579), and at $p\text{H}$ 11.00, calculate $p\text{M}$ when 30.00, 50.00, and 50.02 ml of standard $\text{Na}_2\text{H}_2\text{Y}$ have been added.

Ans. 10.56 (at 50.02 ml).

10. A 50.00-ml portion of 0.0600 M ZnCl_2 is titrated with 0.0400 M $\text{Na}_2\text{H}_2\text{Y}$, in a buffered medium at $p\text{H}$ 6.00. Calculate $p\text{Zn}$ when 74.95, 75.00, and 76.00 ml of the $\text{Na}_2\text{H}_2\text{Y}$ have been added.

11. A 60.0-ml portion of 0.0100 M Na_2PbY is mixed with 35.00 ml of 0.0100 M CuCl_2 . Calculate the concentrations of uncomplexed Cu^{2+} and Pb^{2+} in the mixture.

Ans. $[\text{Pb}^{2+}] = 0.0032 M$, $[\text{Cu}^{2+}] = 0.0004 M$.

12. Calculate E° for the reaction



Does EDTA increase or decrease the oxidizing power of Fe(III) ?

13. A solution contains 0.100 M CaCl_2 and 0.100 M FeCl_3 , and is buffered at $p\text{H}$ 8.00. When an equal volume of 0.100 M $\text{Na}_2\text{H}_2\text{Y}$ is added, show that less than 0.10% of the Fe(III) remains uncomplexed, while less than 0.10% of the Ca(II) is complexed, thereby proving that Fe(III) can be titrated in the presence of Ca(II) .

14. A solution contains CaCl_2 and MgCl_2 . A 50.00-ml aliquot is adjusted to $p\text{H}$ 12, Calcon is added, and the solution is titrated with 0.0563 M $\text{Na}_2\text{H}_2\text{Y}$, 20.63 ml being required. Another 50.00-ml aliquot is buffered at $p\text{H}$ 10 with NH_3 and Erio T is added. Titration to the Erio T end point requires 42.15 ml of the $\text{Na}_2\text{H}_2\text{Y}$. Calculate the concentrations of CaCl_2 and MgCl_2 in the original solution.

15. Calculate the Zn content of a sample, as % ZnCO_3 , that requires 16.52 ml of 0.1000 M EDTA for titration.

Ans. 207.1 mg.

24 THE LITERATURE OF ANALYTICAL CHEMISTRY

There are many thousands of analytical methods and procedures—so many that not even an experienced analyst can know the details of more than a small fraction of them. The analyst depends implicitly on the published literature for the details of these procedures.

As soon as the objective of an analytical problem has been concretely stated, the next step is to discover what has been published concerning this problem. The literature of analytical chemistry is very extensive, but it may be searched systematically.

First, those standard reference books dealing with the problem should be consulted. Some of the many analytical reference books are given in the following list. A reference book in a particular field is usually a good guide to other books and articles in the field; it is for this reason that the number of books in the list is restricted for the most part to ones published recently and in the English language.

If the reference books do not give a satisfactory answer to the problem, the current literature should be investigated, at least from the date of the reference books to the present. At any time, much analytical information appears in the current literature that has not yet been published in reference books.

Although the current literature is widely distributed, it is rather completely classified in *Chemical Abstracts*, published by the American Chemical Society. This semimonthly periodical gives abstracts of articles appearing in over five thousand American and foreign journals of chemistry and its allied subjects. Patents are also abstracted. The

abstracts are grouped by subject into sections, one of which deals with analytical chemistry. The abstracts are indexed noncumulatively each year, according to subject, author, and formula (for organic chemistry). There is also a decennial index. The indexing system is excellent, and cross-indexing is frequent. Instructions for its use may be found in the journal itself, as may directions for obtaining full-length copies of the original articles.

Government bulletins and many publications by manufacturers may also be of analytical interest. Some of these are excellent for special methods, but most are not classified. They are usually discovered indirectly, or by writing to the manufacturer. A list of government publications is obtainable from the Government Printing Office, Washington, D.C.

There are other suggestions which may prove useful in searching the literature:

1. Information in the standard reference books is usually more reliable than that in the current literature, since it has been tested by many individuals over a period of time. However, it is the current literature which contains the latest information. Also, the more recent methods found in the literature are frequently superior to those in reference books. For this reason, even if a satisfactory answer to a problem is found in a reference book, the current literature should still be examined.

2. As soon as a few articles relating to the problem have been found, they should be read before the search is continued; such articles usually contain references to earlier work on the subject. It is for this reason that the search is usually begun with the latest annual index of *Chemical Abstracts*.

3. It is desirable to cultivate the habit of reading current issues of at least one journal. Such reading not only increases one's store of information, but often gives rise to fruitful ideas on one's own work. In the United States the most widely read journal on chemical analysis is *Analytical Chemistry*, published by the American Chemical Society. There are many other excellent analytical periodicals, published in the United States and foreign countries. Some of these journals regularly publish review articles on various topics that are particularly complete and useful.

4. Ordinarily, six months to a year elapses between the completion of an author's work and its publication. About two years pass before the work becomes classified in an annual index of *Chemical Abstracts*. Thus the very latest information is not obtainable from the classified literature. Informal communication is surprisingly effective in overcoming this time lag. Most workers in a particular field make it a policy to attend scientific meetings and to keep in touch with fellow workers. By

corresponding with one's colleagues, or by traveling short distances, it is often possible to find a person who may contribute a great deal of current information to a particular problem.

SELECTED LITERATURE OF ANALYTICAL CHEMISTRY

A. THEORY AND PRACTICE OF QUANTITATIVE ANALYSIS

1. ELEMENTARY TEXTS

- Ayres, G. H., *Quantitative Chemical Analysis*. Harper, New York, 1958.
- Belcher, R., and Nutten, A. J., *Quantitative Inorganic Analysis*. Butterworths, London, 1960.
- Charlot, G., and Bezier, D., *Quantitative Inorganic Analysis*. Wiley, New York, 1957.
- Day, R. A., and Underwood, A. L., *Quantitative Analysis*. Prentice-Hall, Englewood Cliffs, N.J., 1958.
- Diehl, H., and Smith, G. F., *Quantitative Analysis: Elementary Principles and Practice*. Wiley, New York, 1952.
- Hamilton, L. F., and Simpson, S. G., *Calculations of Analytical Chemistry*, 6th ed. McGraw-Hill, New York, 1960.
- Kolthoff, I. M., and Sandell, E. B., *Textbook of Quantitative Inorganic Analysis*, 3d ed. Macmillan, New York, 1952.
- Macdonald, A. M. G., *Elementary Titrimetric Analysis*. Butterworths, London, 1960.
- Olson, A. R., Koch, C. W., and Pimentel, G. C., *Introductory Quantitative Chemistry*. Freeman, San Francisco, 1956.
- Pierce, W. C., Haenisch, E. L., and Sawyer, D. T., *Quantitative Analysis*, 4th ed. Wiley, New York, 1958.
- Vogel, A. I., *A Textbook of Quantitative Inorganic Analysis*, 3d ed. Wiley, New York, 1961.

2. ADVANCED TEXTS

- Kolthoff, I. M., and Elving, P. J. (eds.), *Treatise on Analytical Chemistry*. Wiley, New York, 1959—. 10 vols.
- Kolthoff, I. M., and Stenger, V. A., *Volumetric Analysis*, 2d ed. Wiley, New York, 1942-57. 3 vols.
- Laitinen, H. A., *Chemical Analysis*. McGraw-Hill, New York, 1960.
- Lundell, G. E. F., and Hoffman, J. I., *Outlines of Methods of Chemical Analysis*. Wiley, New York, 1938.
- Meites, L., and Thomas, H. C., *Advanced Analytical Chemistry*. McGraw-Hill, New York, 1958.
- Smith, T. B., *Analytical Processes: A Physico-Chemical Interpretation*, 2d ed. Arnold, London, 1952.
- Strouts, C. R. N., Gilfillan, J. H., and Wilson, H. N. (eds.), *Analytical Chemistry*. Oxford University Press, New York, 1955. 2 vols.
- Wagner, W., Hull, C. J., and Markle, G. E., *Advanced Analytical Chemistry*. Reinhold, New York, 1956.
- Walton, H. F., *Principles and Methods of Chemical Analysis*. Prentice-Hall, Englewood Cliffs, N.J., 1952.
- Wilson, C. L., and Wilson, D. W. (eds.), *Comprehensive Analytical Chemistry*. Am. Elsevier, New York, 1959—. 7 vols.

3. BOOKS ON SPECIAL SUBJECTS

- Alders, L., *Liquid-Liquid Extraction*, 2d ed. Am. Elsevier, New York, 1959.
- Bates, R. G., *Electrometric pH Determinations*. Wiley, New York, 1954.
- Bauman, R. P., *Absorption Spectroscopy*. Wiley, New York, 1962.
- Benedetti-Pichler, A. A., *Introduction to the Microtechnique of Inorganic Analysis*. Wiley, New York, 1942.
- Block, R. J., and Zweig, G., *A Practical Manual of Paper Chromatography and Electrophoresis*. Academic Press, New York, 1962.
- Clark, S. J., *Quantitative Methods of Organic Microanalysis*. Butterworths, London, 1956.
- Critchfield, F. E., *Organic Functional Group Analysis*. Pergamon Press, New York, 1962.
- Duval, C., *Inorganic Thermogravimetric Analysis*. Elsevier, Amsterdam, Houston, 1953.
- Evers, N., and Smith, W., *Analysis of Drugs and Chemicals*. Griffin, London, 1955.
- Flaschka, H., *EDTA Titrations*. Pergamon Press, New York, 1959.
- Fritz, J. S., and Hammond, G. S., *Quantitative Organic Analysis*. Wiley, New York, 1957.
- Glick, D. (ed.), *Methods of Biochemical Analysis*. Wiley, New York, 1954—. 11 vols.
- Headridge, J. B., *Photometric Titrations*. Pergamon Press, New York, 1961.
- Heftmann, E., *Chromatography*. Reinhold, New York, 1961.
- Higuchi, T., and Brockmann-Hanssen, E. (eds.), *Pharmaceutical Analysis*. Wiley, New York, 1961.
- Ives, D. J. G., and Janz, G. J. (eds.), *Reference Electrodes*. Academic Press, New York, 1961.
- Jackson, M. L., *Soil Chemical Analysis*. Prentice-Hall, Englewood Cliffs, N.J., 1958.
- Jenkins, G. L., Christian, J. E., and Hager, G. P., *Quantitative Pharmaceutical Chemistry*, 5th ed. McGraw-Hill, New York, 1957.
- Kirk, P. L., *Quantitative Ultramicroanalysis*. Wiley, New York, 1950.
- Kolthoff, I. M., and Elving, P. J. (eds.), *Treatise on Analytical Chemistry*. Wiley, New York, 1959—. 10 vols.
- Lamb, C. A., Bentley, O. G., and Beattie, J. M. (eds.), *Trace Elements*. Academic Press, New York, 1958.
- Lingane, J. J., *Electroanalytical Chemistry*, 2d ed. Wiley, New York, 1958.
- Mattock, G., *pH Measurement and Titration*. Macmillan, New York, 1961.
- Meites, L., *Polarographic Techniques*. Wiley, New York, 1955.
- Mellon, M. G., *Analytical Absorption Spectroscopy*. Wiley, New York, 1950.
- Milner, G. W. C., *The Principles and Applications of Polarography and Other Electroanalytical Processes*. Wiley, New York, 1957.
- Milton, R. F., and Waters, W. A., *Methods of Quantitative Micro-chemical Analysis*, 2d ed. St. Martins, New York, 1955.
- Mitchell, J., Jr., Kolthoff, I. M., Proskauer, E. S., and Weissberger, A. (eds.), *Organic Analysis*. Wiley, New York, 1953-60. 4 vols.
- Morrison, G. H., and Freiser, H., *Solvent Extraction in Analytical Chemistry*. Wiley, New York, 1957.

- Mullen, P. W., *Modern Gas Analysis*. Wiley, New York, 1955.
- Orr, C., Jr., and DallaValle, J. M., *Fine Particle Measurement*. Macmillan, New York, 1959.
- Phillips, J. P., *Automatic Titrators*. Academic Press, New York, 1959.
- Reilley, C. N. (ed.), *Advances in Analytical Chemistry and Instrumentation*. Wiley, New York, 1960—. 2 vols.
- Samuelson, O., *Ion Exchangers in Analytical Chemistry*, 2d ed. Wiley, New York, 1962.
- Schaeffer, H. F., *Microscopy for Chemists*. Van Nostrand, New York, 1953.
- Siggia, S., and Stolten, H. J., *An Introduction to Modern Organic Analysis*. Wiley, New York, 1956.
- Smale, A. A., and Wager, L. R., *Methods in Geochemistry*. Wiley, New York, 1960.
- Smith, O. C., *Identification and Qualitative Chemical Analysis of Minerals*, 2d ed. Van Nostrand, New York, 1953.
- Steyermark, A., *Quantitative Organic Microanalysis*, 2d ed. Academic Press, New York, 1961.
- Sutton, F., *Systematic Handbook of Volumetric Analysis*, 13th ed. Butterworths, London, 1955.
- Tine, G., *Gas Sampling and Chemical Analysis in Combustion Processes*. Pergamon Press, New York, 1961.
- Tomicek, O., *Chemical Indicators*. Academic Press, New York, 1951.
- Udenfriend, S., *Fluorescence Assay in Biology and Medicine*. Academic Press, New York, 1962.
- Umbreit, W. W., Burris, R. H., and Stauffer, J. F., *Manometric Techniques*. Burgess, Minneapolis, 1957.
- Wallis, T. E., *Analytical Microscopy*, 2d ed. Little, Brown, Boston, 1957.
- Weisz, H., *Microanalysis by the Ring Oven Technique*. Pergamon Press, New York, 1961.
- Welcher, F. J., *The Analytical Uses of Ethylenediaminetetraacetic Acid*. Van Nostrand, New York, 1957.
- Yoe, J. H., and Koch, H. J., *Trace Analysis*. Wiley, New York, 1957.

B. APPLIED ANALYSIS

- Ahrens, L. H., *Quantitative Spectrochemical Analysis of Silicates*. Addison-Wesley, Reading, Mass., 1954.
- Boltz, D. F. (ed.), *Colorimetric Determination of Nonmetals*. Wiley, New York, 1958.
- Browne, C. A., and Zerban, F. W., *Physical and Chemical Methods of Sugar Analysis*, 3d ed. Wiley, New York, 1941.
- Busev, A. I., *The Analytical Chemistry of Indium*. Pergamon Press, New York, 1962.
- Churchill, H. V., and Bridges, R. W., *Chemical Analysis of Aluminum*, 3d ed. Aluminum Company of America, New Kensington, Pa., 1950.
- Cox, H. E., and Pearson, D., *Chemical Analysis of Foods*. Tudor, New York, 1962.
- Davis, J. G., *Milk Testing*, 2d ed. Dairy Industries, Ltd., London, 1959.
- Dozinal, C. M., *Modern Methods of Analysis of Copper and Its Alloys*. G. Thone, Liege, Belgium, 1960.
- Elwell, W. T., and Wood, D. F., *The Analysis of Titanium, Zirconium, and Their Alloys*. Wiley, New York, 1961.

- Feigl, F., *Spot Tests in Inorganic Analysis*, 6th ed. Am. Elsevier, New York, 1960.
- Fresenius, R., and Jander, G., *Handbuch der analytischen Chemie*. J. Springer, Berlin, 1940—. 19— vols.
- Groves, A. W., *Silicate Analysis*, 2d ed. Allen and Unwin, London, 1951.
- Gunther, F. A., and Blinn, R. C., *Analysis of Insecticides and Acaricides*. Wiley, New York, 1955.
- Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2d ed. Wiley, New York, 1953.
- Hills, F. G., *The Technical Analysis of Ores and Metallurgical Products*. Tudor, New York, 1937.
- Jacobs, M. B., *The Analytical Chemistry of Industrial Poisons, Hazards, and Solvents*, 2d ed. Wiley, New York, 1949.
- Jacobs, M. B., *The Chemical Analysis of Air Pollutants*. Wiley, New York, 1960.
- Jacobs, M. B., *Chemical Analysis of Foods and Food Products*, 3d ed. Van Nostrand, New York, 1958.
- Jacobs, M. B., and Scheffan, L., *Chemical Analysis of Industrial Solvents*. Wiley, New York, 1953.
- Kappelmeyer, C. P. A. (ed.), *Chemical Analysis of Resin-Based Coating Materials*. Wiley, New York, 1959.
- Kolthoff, I. M., and Elving, P. J. (eds.), *Treatise on Analytical Chemistry*. Wiley, New York, 1959—. 10 vols.
- Mattiello, J. J., *Protective and Decorative Coatings*, Vol. V (Analysis and Testing Methods). Wiley, New York, 1946.
- Mitchell, J., Jr., and Smith, D. M., *Aquametry*. Wiley, New York, 1948.
- Norwitz, G., *Rapid Analysis of Nonferrous Metals and Alloys*. Tudor, New York, 1957.
- Noyes, A. A., and Bray, W. C., *A System of Qualitative Analysis for the Rare Elements*. Macmillan, New York, 1927.
- Pigott, E. C., *Ferrous Analysis: Modern Practice and Theory*, 2d ed. Wiley, New York, 1953.
- Piper, C. S., *Soil and Plant Analysis*. Wiley, New York, 1944.
- Rainwater, F. H., and Thatcher, L. L., *Methods for Collection and Analysis of Water Samples*. U.S. Geological Survey Paper No. 1454, U.S. Govt. Printing Office, 1960.
- Rodden, C. J. (ed.), *Analytical Chemistry of the Manhattan Project*. McGraw-Hill, New York, 1950.
- Rosen, M. J., and Goldsmith, H. A., *Systematic Analysis of Surface-Active Agents*. Wiley, New York, 1960.
- Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3d ed. Wiley, New York, 1959.
- Schoeller, W. R., and Powell, A. R., *The Analysis of Minerals and Ores of the Rarer Elements*, 3d ed. Hafner, New York, 1956.
- Snell, F. D., Snell, C. T., and Snell, C. A., *Colorimetric Methods of Analysis*, Vol. IIIA. Van Nostrand, New York, 1961.
- Swift, E. H., *A System of Chemical Analysis for the Common Elements*. Freeman, San Francisco, 1939 (reissued, 1955).
- Versagi, F. J., *Routine Analysis of Copper Base Alloys*. Tudor, New York, 1960.
- Vickery, R. C., *Analytical Chemistry of the Rare Earths*. Pergamon Press, New York, 1960.

Welcher, F. J., *Organic Analytical Reagents*. Van Nostrand, New York, 1947-48. 4 vols.

Westwood, W., and Mayer, A., *Chemical Analysis of Cast Iron and Foundry Materials*, 2d ed. Allen and Unwin, London, 1960.

Young, R. S., *Industrial Inorganic Analysis*. Wiley, New York, 1953.

C. OFFICIAL METHODS AND PROCEDURES PUBLISHED BY PROFESSIONAL ORGANIZATIONS*

American Association of Clinical Chemists, *Standard Methods of Clinical Chemistry*. Academic Press, New York, 1958—. 3— vols.

American Association of Feed Microscopists, *Manual of Microscopic Analysis of Feeding Stuffs*. Missouri State Dept. of Agriculture, Jefferson City, Mo., 1961.

American Conference of Governmental Industrial Hygienists, *Manual of Analytical Methods Recommended for Sampling and Analysis of Atmospheric Contaminants*. Cincinnati, Ohio, 1958.

American Pharmaceutical Association, *Pharmacopoeia of the United States*, 16th ed. Mack Publishing Co., Easton, Pa., 1960.

American Public Health Association, *Standard Methods for the Examination of Water, Sewage, and Industrial Wastes*, 10th ed. New York, 1955.

American Society for Testing and Materials, *ASTM Standards*. Philadelphia, 1955.

American Society for Testing and Materials, *ASTM Standards on Methods of Atmospheric Sampling and Analysis*. Philadelphia, 1959.

American Society for Testing and Materials, *Book of ASTM Methods for Chemical Analysis of Metals*. Philadelphia, 1960.

Association of Official Agricultural Chemists, *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 9th ed. (W. Horwitz, ed.). Washington, D.C., 1960.

Association of Vitamin Chemists, *Methods of Vitamin Assay*, 3d ed. Wiley, New York, 1961.

Society for Analytical Chemistry, *Methods for the Analysis of Nonsoapy Detergent Products* (SAC Monograph No. 1). London, 1961.

D. PHYSICAL AND CHEMICAL DATA

American Chemical Society, *Reagent Chemicals: American Chemical Society Specifications*, 1955. Washington, D.C., 1955.

Bjerrum, J., Schwarzenbach, G., and Sillen, G., *Stability Constants*. Special Publication No. 7. The Chemical Society, London, 1957-58. 2 vols.

Charlot, G., *Selected Constants: Oxido-Reduction Potentials*. Pergamon Press, New York, 1958.

Hodgeman, C. D. (ed.), *Handbook of Chemistry and Physics*, 43d ed. Chemical Rubber Co., Cleveland, Ohio, 1962.

Lange, N. A., *Handbook of Chemistry*, 10th ed. McGraw-Hill, New York, 1961.

Merck and Co., *The Merck Index of Chemicals and Drugs*, 7th ed. Rahway, N.J., 1960.

*Considered to be the most reliable methods.

Rosin, J., *Reagent Chemicals and Standards*, 4th ed. Van Nostrand, New York, 1961.

Seidell, A., *Solubilities of Inorganic and Metal Organic Compounds*, 4th ed. (W. F. Linke, ed.). Van Nostrand, New York, 1958.

U.S. National Research Council, *International Critical Tables of Numerical Data*. McGraw-Hill, New York, 1926-33. 7 vols.

E. INSTRUMENTAL METHODS*

Berl, W. G. (ed.), *Physical Methods in Chemical Analysis*. Academic Press, New York, 1950-61. 4 vols.

Weissberger, A. (ed.), *Technique of Organic Chemistry*, 3d ed. Wiley, New York, 1959—.

F. PERIODICALS AND SPECIAL BULLETINS†

*See Chapter 22.

†See text.

SUPPLEMENT

MATHEMATICS ESSENTIAL TO QUANTITATIVE ANALYSIS

ADDITIONAL METHODS OF SOLVING ALGEBRAIC EQUATIONS BY APPROXIMATIONS

(See Sec. 3B, p. 16)

Method of Successive Approximations

For a particular case, the method of neglecting small quantities may give an approximate answer that is not of the desired accuracy, but neither is it highly erroneous. In this case, the first approximate value may be used to give a second, better approximation. This process may be repeated until two successive values are obtained that are identical within the required precision, and that may be taken as the correct value. After the student has acquired some experience, this method is often faster than the quadratic formula.

Example. Calculate x , a concentration that cannot be negative, from the equation

$$\frac{x(0.0100 + x)}{(0.0100 - x)} = 0.00050$$

First approximation: Assume x negligible compared to 0.0100.

$$\frac{x_1(0.0100 + x)}{(0.0100 - x)} = 0.00050 \quad \text{or} \quad x_1 = 0.00050$$

The quantity x_1 is about 5% of the quantity 0.0100, and is not negligible. As a *second approximation*, therefore, it would be better to estimate the quantities $(0.0100 + x)$ and $(0.0100 - x)$ as $(0.0100 + 0.0005)$ and $(0.0100 - 0.0005)$, respectively.

$$\frac{x_2(0.0100 + 0.0005)}{(0.0100 - 0.0005)} = 0.00050 \quad \text{or} \quad x_2 = 0.00045$$

Third approximation:

$$\frac{x_3(0.0100 + 0.00045)}{(0.0100 - 0.00045)} = 0.00050 \quad \text{or} \quad x_3 = 0.00046$$

Fourth approximation:

$$\frac{x_4(0.0100 + 0.00046)}{(0.0100 - 0.00046)} = 0.00050 \quad \text{or} \quad x_4 = 0.00046$$

Since the third and fourth estimates are identical within the required precision, the answer is 0.00046. The fourth estimate really need not be made; from the rate of convergence, a comparison of the second and third estimates shows that the fourth will be the same as the third.

Trial-and-Error Method

It is not always possible or convenient to use the method of successive approximations, for it does require some insight into the problem. The trial-and-error method is generally applicable to the numerical solution of any equation in a single unknown. The time required is usually greater than for the preceding systematic methods, but this may be unimportant. Where the other procedures fail, and a solution must be obtained, the trial-and-error method (or a more rigorous approximation procedure similar to it) must be used.

All equations containing x as a single unknown may be put into the form

$$f(x) = 0$$

Any value of x that makes $f(x) = 0$ is a solution to the equation. Such a value may be found by trial and error as follows. First, values of $f(x)$ are computed for a few integral values of x , until one value of x is found which makes $f(x)$ positive, and another value of x is found which makes $f(x)$ negative. These two values of x bracket the root of the equation. The bracketing range is then narrowed by making successively refined guesses at x and calculating the corresponding values of $f(x)$. When an x value is found that makes $f(x) = 0$ within the required precision, this value is a solution of the equation. With a little practice, this method is quite rapid. On the average, about two estimates are needed per decimal place in the answer.

Example. To the third decimal place, find the real positive roots of the equation

$$x^3 + \log x - 2.350 = 0$$

The answer is arrived at by calculating values of $f(x)$ for various values of x , as shown in the following table. Comments are included where necessary, so that the student may understand the reasoning in passing from one step to the next.

x	$f(x)$	Comments
0.....	$-\infty$	
1.....	-1.35	$f(x)$ decreases continuously below 1. All positive roots are above 1.
2.....	+5.95	$f(x)$ increases rapidly and continuously above 2. All positive roots are below 2. Next guess should be closer to 1 than to 2.
1.2.....	-0.542	
1.3.....	-0.040	Because $f(x)$ increases rapidly with increasing x , the next estimate should be closer to 1.3 than to 1.4.
1.32.....	+0.070	Overestimated. Closer to 1.30 than to 1.32.
1.305.....	-0.010	
1.307.....	-0.001	Either 1.306 or 1.308 would be poorer answers. The equation has no other positive roots.

SUPPLEMENTARY PROBLEMS

Section 3B

Solve each of the following equations for the positive values of x .

S1. $x^2(x + 0.010) = 1.00 \times 10^{-8}$ *Ans.* 0.097.

S2. $x^2(x + 0.010) = 1.00 \times 10^{-8}$

S3. $x^2 + \log x^4 = 0$ *Ans.* 0.733....

S4. $(2 + x)^2 + \log x = 8.033$

S5. $x + \sin 2\pi x + 0.151 = 0$ *Ans.* 0.647, 0.800.

S6. $x + 2 \log x + \sin 2\pi x - 0.093 = 0$

THE THEORY OF ERROR AND THE TREATMENT OF QUANTITATIVE DATA

QUANTITATIVE PROPERTIES OF THE NORMAL DISTRIBUTION

(See Sec. 5C.1, p. 42)

Equation of the Normal Curve

The equation of the normal curve shown in Fig. 5.2 (p. 43) is

$$Y = e^{-\frac{1}{2}[(X - \mu)/\sigma]^2}$$

where X is the abscissa, indicating the magnitude of the measurement.

Y is the ordinate, indicating the relative frequency of occurrence of the measurement. Y is arbitrarily taken as unity for the most probable value, $X = \mu$.

e is the base of natural logarithms, 2.7183....

μ is a parameter of the curve, and represents the true value of the quantity being measured. μ is the value of X at the maximum of the curve.

σ is the true standard deviation, a second parameter of the curve, which determines the sharpness of the peak.

The three scales of abscissae in Fig. 5.2 require elucidation. The upper scale represents the actual value (X) of the measurement. If the true value (μ) of the quantity is subtracted from each value of X , the curve also represents the distribution of errors ($X - \mu$) about the true value, as shown by the middle scale of abscissae. Thus each point on the locus represents the relative frequency of occurrence of a measurement whose magnitude is given by X (upper scale of abscissae), or whose error is given by $X - \mu$ (middle scale of abscissae). In the lowest scale, the units of error, instead of being given in the same units as X (i.e., cm, g, %, etc.), are given in standard deviation units, or σ units, $(X - \mu)/\sigma$. Being ratios, σ units are dimensionless. When σ units are used, the same curve describes all normal sets of measurements, regardless of the numerical values of μ and σ .

Relative Frequencies of Occurrence of Single Measurements

Figure 5.2 is drawn to scale, and the lengths of the ordinates represent the relative frequencies of occurrence of certain values of X , or of certain errors. Thus ordinates at errors of 0 , $\pm\sigma$, $\pm2\sigma$, and $\pm3\sigma$ are in the ratios $1.00:0.61:0.14:0.01$, which ratios therefore represent the relative frequencies of occurrence of these errors. The relative lengths of the ordinates of the normal curve may be found more precisely from a table of ordinates like that in Appendix IIA (p. 908).

It should be noted that the true value ($X = \mu$) has a better chance of occurrence than any other single value of X . This does not mean, however, that the true value has a better chance of occurrence than *all* other values together.

Probability of a Measurement Falling within a Certain Range

The ratio of the area between any two ordinates under the normal curve to the total area under the curve represents the fraction of the total measurements that lies between the error limits set by the two ordinates. Extensive tables may be found in the literature that give areas between ordinates. Appendix IIB (p. 909) is such a table. Some of the information in Appendix IIB is presented in approximate form in Figs. 5.2 and S5.1.

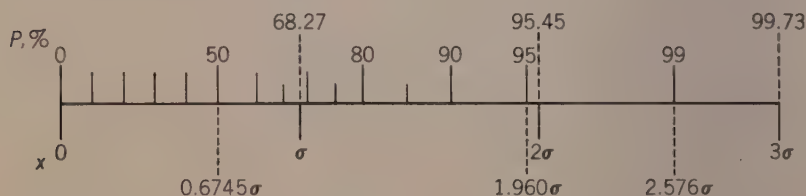


FIG. S5.1. Probability of Occurrence of Errors or Deviations— P is the percentage of a large number of determinations falling within the range $\pm x$ about the true value. P may also be interpreted as the probability that a single determination will fall within the range $\pm x$ about the true value. (Reprinted, with permission of the American Society for Testing and Materials, from *ASTM Manual on Quality Control of Materials*, Special Technical Publication 15-C, 1951.)

From Fig. S5.1 it may be seen that 50% of all measurements fall within 0.6745σ of the true value; 68.27% (approximately two-thirds) fall within 1σ of the true value; only about 5% of the observations fall outside the error range of -2σ to $+2\sigma$; and only about 0.3% fall outside the error range of -3σ to $+3\sigma$. These relationships are summarized in Fig. 5.2.

Another way of interpreting the statements of the preceding paragraph is to say that a worker may be fairly sure that a single measurement will fall within a rather wide range about the true value; but that as the range is narrowed, he has less assurance that any single measurement will fall therein. This interpretation is made clear in the following examples, which also illustrate use of the table of areas in Appendix IIB.

Example S1. The true value of a quantity is 20.00 cm, and σ for the method of measurement is 0.20 cm. What is the probability that a single measurement will have an error greater than 0.30 cm (i.e., fall outside the range 20.00 ± 0.30 cm)?

$$\text{Error, in } \sigma \text{ units} = \frac{0.30}{0.20} = 1.5$$

Approximately, from Fig. S5.1, P for $x = 1.5\sigma$ is about 85%, meaning that about 15% of the measurements will fall outside the range $\pm 1.5\sigma$ about the mean, or outside the range 20.00 ± 0.30 cm.

Precisely, from Appendix IIB, the area under the normal curve from 0 to 1.5σ is 0.43319, meaning that 43.319% of the measurements will fall within the range 0 to 1.5σ . Hence 2×43.319 , or 86.638% of the measurements, will fall within the range -1.5σ to $+1.5\sigma$. Therefore the percentage of measurements falling outside this range is $100 - 86.638$, or 13.362%.

Note that the area corresponding to a particular ordinate is very precisely given in the table of areas. In this example, however, the error in σ units has an uncertainty of about 1 in 15. That is, the error could lie between 1.4 and 1.6σ units, and the corresponding areas could lie between 84% and 89%. In this example, therefore, it is not justifiable to give the area to more than two significant figures, or 87%.

Example S2. Suppose that a worker regards as too high the 13% probability of Ex. S1 that a single measurement will fall outside the specified range 20.00 ± 0.30 cm. He wishes to specify a range sufficiently broad that there is only a 2.0% probability that a single measurement will fall outside. What must this range be?

Approximately, from Fig. S5.1, for $P = 100 - 2 = 98\%$, x is about 2.3σ , or $(2.3)(0.20) = 0.46$ cm. Hence the range within which 98% of the determinations fall is 20.00 ± 0.46 cm.

More precisely, from Appendix IIB, $(X - \mu)/\sigma$ for $0.980/2 = 0.490$ of the total area is 2.33. Hence $X - \mu = 2.33\sigma = (2.33)(0.20)$ cm = 0.47 cm. Hence the range within which 98% of the measurements fall is 20.00 ± 0.47 cm.

The Standard Deviation and Its Distribution

The normal curve falls off less rapidly for large values of σ than for small values, as may be seen from the equation of the curve. Therefore, σ is a measure of precision.

As with μ , σ cannot be exactly known unless it can be estimated from an infinitely large set of measurements. For a finite number of measure-

ments, s is the best estimate of σ . The larger N is, the more reliable the estimate. Both s and σ are called “standard deviation” by statisticians; therefore, to avoid confusion, the symbols s and σ are used in the text, instead of the words “standard deviation.” The distinction between the calculable estimate s and the true σ must always be kept in mind.

Suppose that a large number of sets of measurements of N individuals each is taken on the same quantity by the same method, and s calculated for each set. In general, the observed s differs from set to set and is not equal to σ (except by chance). Values of s are *distributed* about σ in a way that has been thoroughly studied, and this distribution is summarized for sets with $N = 4$ and $N = 9$ in Fig. S5.2.

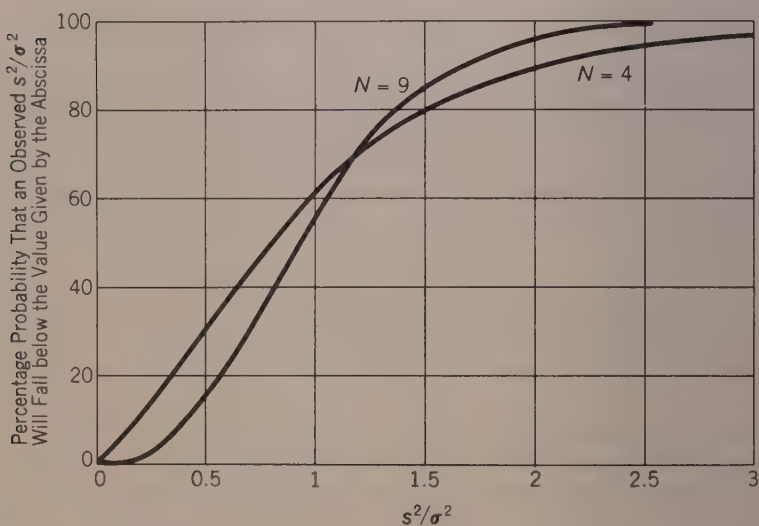


FIG. S5.2. Distribution of s^2/σ^2 for $N = 4$ and $N = 9$

This figure may be interpreted as follows. When s is calculated from a set of four measurements, there is a 95% probability that s^2/σ^2 will be 2.6 or lower. There is a 5% probability that s^2/σ^2 will be 0.12 or lower. Consequently, there is a 90% probability that an observed s^2/σ^2 will fall in the range 0.12 to 2.6, and a 10% probability that s^2/σ^2 will fall outside this range. Similar statements may be made for other probability levels. In other words, s may vary considerably from one set of measurements to another, and s is not a precise estimate of σ when the sets are small. Comparison of the two curves shows that the range within which s^2/σ^2 may fall with a 90% probability is narrower for $N = 9$

than for $N = 4$; thus as N becomes larger, s becomes a better estimate of σ .

For reasons that will become apparent later, the regions of principal interest are at the ends of the distribution curves. Table S5.1 gives values of s^2/σ^2 at certain extreme probability levels more precisely than Fig. S5.2, and more values of N are included. The use of Table S5.1 is illustrated in the following examples.

TABLE S5.1
DISTRIBUTION OF THE RATIO s^2/σ^2

Number of Measurements in the Set from Which s Is Computed	Per Cent Probability That s^2/σ^2 Is below the Limiting Value Shown							
	1%	2.5%	5%	10%	90%	95%	97.5%	99%
2	0.0002	0.001	0.004	0.0158	2.71	3.84	5.02	6.63
3	0.010	0.025	0.051	0.105	2.30	3.00	3.69	4.61
4	0.038	0.072	0.117	0.195	2.08	2.60	3.12	3.78
5	0.074	0.121	0.178	0.266	1.94	2.37	2.79	3.32
6	0.111	0.166	0.229	0.322	1.85	2.21	2.57	3.02
7	0.145	0.206	0.273	0.367	1.77	2.10	2.41	2.80
8	0.177	0.241	0.310	0.405	1.72	2.01	2.29	2.64
9	0.206	0.272	0.342	0.436	1.67	1.94	2.19	2.51
10	0.232	0.300	0.369	0.463	1.63	1.88	2.11	2.41
12	0.278	0.347	0.416	0.507	1.57	1.79	1.99	2.25
14	0.316	0.385	0.453	0.542	1.52	1.72	1.90	2.13
16	0.349	0.417	0.484	0.570	1.49	1.67	1.83	2.04
18	0.377	0.445	0.511	0.594	1.46	1.63	1.78	1.97
20	0.402	0.468	0.532	0.613	1.43	1.59	1.73	1.91
25	0.452	0.517	0.577	0.652	1.38	1.52	1.64	1.79
30	0.490	0.552	0.610	0.681	1.35	1.47	1.58	1.71
40	0.549	0.607	0.659	0.721	1.30	1.40	1.49	1.60
60	0.622	0.672	0.717	0.771	1.24	1.32	1.39	1.48
120	0.721	0.762	0.797	0.838	1.17	1.22	1.27	1.33
∞	1.000	1.000	1.000	1.000	1.00	1.00	1.00	1.00

Example S1. For a certain method of measurement on a certain quantity, σ is 2.00. What is the range within which s , as calculated from a set of 6 measurements, may be expected to fall 90% of the time?

From Table S5.1, for 6 measurements, s^2/σ^2 may be expected to fall at 0.229 or less with a 5% probability, and at 2.21 or above with a 5% probability.

Thus in 90% of the cases, $0.229 \leq s^2/\sigma^2 \leq 2.21$.

Solving for s , we obtain

$$\begin{aligned}\sigma\sqrt{0.229} &\leq s \leq \sigma\sqrt{2.21}, \text{ or} \\ 2.00\sqrt{0.229} &\leq s \leq 2.00\sqrt{2.21} \\ 0.957 &\leq s \leq 2.97\end{aligned}$$

It may be seen that even if the extreme 10% of observed s values is rejected, the remaining 90% varies over a rather wide range (threefold).

Example S2. When calculated from a set of 4 measurements, s is 0.100. Within what limits does σ probably lie?

Before this question is answered, it is necessary to settle on the degree of confidence that may be put in the answer. If we wanted to be very sure that σ lay within the stated limits, the range would have to be very wide. If we are satisfied with a 95% probability of being correct (i.e., a 5% probability of being wrong), then for sets of 4 measurements, from Table S5.1, $0.072 \leq s^2/\sigma^2 \leq 3.12$.

Solving for σ , we obtain

$$\begin{aligned}1/0.072 &\geq \sigma^2/s^2 \geq 1/3.12 \\ s/\sqrt{0.072} &\geq \sigma \geq s/\sqrt{3.12} \\ 0.373 &\geq \sigma \geq 0.057\end{aligned}$$

It may be seen that if we wish to be reasonably certain that σ lies within the given range, the range cannot be very precisely stated when estimated from a small number of measurements. Even for the wide (sevenfold) range given above, we will be wrong 5% of the time, and σ will not lie in the stated range.

The Mean and Its Distribution

If a large number of groups of measurements is obtained, each group containing N measurements, the computed means of the group are generally not identical, but are scattered about the true value. However, the scattering of the means is less than that of the individual measurements. The standard deviation, σ_m , of the distribution of means is related to the σ of a single measurement constituting that mean:

$$\sigma_m = \sigma/\sqrt{N}$$

This equation is very important, since it allows computation of the σ of the mean from the σ of the single measurements that compose the mean.

The scattering of means is depicted in Fig. S5.3. The first inference that may be made from the foregoing equation and Fig. S5.3 is that it is desirable to make as many determinations as possible in order to reduce the random error of a mean. Thus when determinations are simple, as they are if only a few scale or dial readings are involved, they are usually performed many times. Millikan's determination of the charge of the electron is a classical example of the use of a great number

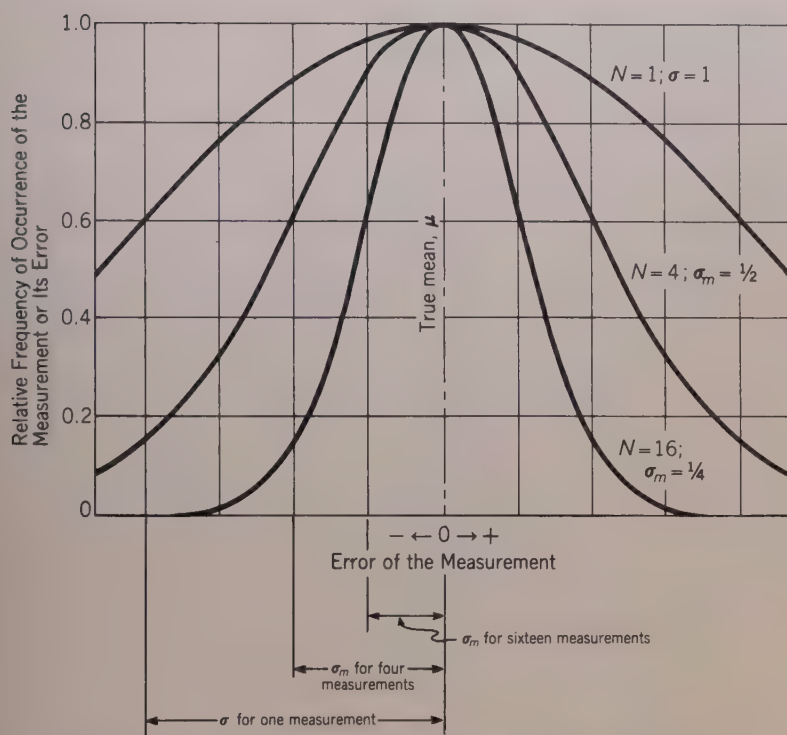


FIG. S5.3. Scattering of Means and Individual Measurements about the True Value

of observations to increase the precision of a measurement. Literally hundreds of measurements were taken and averaged to achieve a reliable mean value for the charge.

However, a second inference may also be drawn from the inverse square root relationship between σ_m and N : the point of diminishing returns is soon reached, where the increase in precision obtained by increasing the number of measurements is not worth the additional effort required. Thus, if there is a certain random error associated with one determination, this error may be halved by taking a mean of four determinations. But in order to halve the error again, a total of sixteen determinations must be made; that is, twelve more determinations must be made to give another twofold reduction of the random error.

Of course, very few experimental errors may be reduced without limit simply by increasing N . Almost all experimental errors are partly determinate, and the determinate part cannot be reduced simply by increasing N .

Example S1. What are the standard deviations of the means obtained from 2, 4, and 9 determinations, if σ for a single determination is 0.30%?

The value of σ_m for the mean of 2 determinations is $0.30/\sqrt{2} = 0.21\%$.

Values of σ_m for means of 4 and 9 determinations are, respectively, $0.30/\sqrt{4} = 0.15\%$ and $0.30/\sqrt{9} = 0.10\%$.

Example S2. The σ of a single determination is 0.30 cm. (a) What is the probability that a mean of 4 determinations will fall within 0.45 cm of the true value? (b) What is the probability that a mean of 4 determinations will fall more than 0.45 cm above the true value? (c) Within what range of the true value will 99% of the means of 4 determinations fall? (d) How many replicate determinations would have to be made in order that their mean would fall within 0.20 cm of the true value 99% of the time?

(a) The value of σ_m for 4 determinations is $\frac{\sigma}{\sqrt{N}} = \frac{0.30}{\sqrt{4}} = 0.15$ cm. Then 0.45 cm $= \frac{0.45}{0.15} \sigma_m = 3.0\sigma_m$.

From Appendix IIB, the probability of a mean falling within the range 0 to $3.0\sigma_m$ is 49.865%. Hence the probability of a mean falling within the range $-3.0\sigma_m$ to $3.0\sigma_m$ (i.e., -0.45 to 0.45 cm about the true value) is $2 \times 49.865\%$, or 99.730%.

(b) From part a, the probability of a mean falling within 0 to 0.45 cm of the true value is 49.865%. Hence the probability of a mean falling higher than 0.45 cm above the true value is $50 - 49.865$, or 0.135%.

(c) From Appendix IIB, $X - \mu$ for 0.99/2 of the total area is 2.576σ . Hence $\bar{X} - \mu = 2.576\sigma_m = 2.576(0.15) = 0.39$ cm. The range within which 99% of the means fall is therefore ± 0.39 cm about the true value.

(d) If one wishes to specify that a mean should fall within a certain range of the true value, then N must be made large enough to meet this specification.

From Appendix IIB, $X - \mu$ for 0.99/2 of the total area is 2.576σ . Hence,

$$\begin{aligned}\bar{X} - \mu &= 2.576\sigma_m \\ \sigma_m &= \frac{\bar{X} - \mu}{2.576} = \frac{0.20}{2.576} = 0.078\end{aligned}$$

To find N ,

$$\begin{aligned}\sigma_m &= \frac{\sigma}{\sqrt{N}} \\ N &= \frac{\sigma^2}{\sigma_m^2} = \frac{0.30^2}{0.078^2} = 14.9, \text{ or } 15\end{aligned}$$

USEFUL STATISTICAL TESTS

(See Sec. 5C.3, p. 45)

In the preceding sections the distributions of single measurements, of means, and of s were described in an attempt to give the student an introduction to statistical principles. In the following sections some statistical tests are given that aid in the interpretation of experimental measurements.

Confidence Limits for the Mean

With the realization that \bar{X} is only an estimate of μ , the question arises as to how close the measured \bar{X} lies to μ . This question may be answered statistically by defining an interval about \bar{X} , within which interval one may with a certain degree of confidence expect μ to lie.

The more confident one wishes to be that μ lies within the stated interval, the broader this interval must be. The interval so defined is called a *confidence interval*, its limits are called *confidence limits*, and the percentage probability that μ lies within this interval is called the *confidence level*. The *error probability* ($100 - \text{confidence level}$) is the per cent probability that μ will lie outside the confidence interval, and represents the chances of being incorrect in stating that μ lies within the confidence interval.

When σ is known, the table of areas may be used to estimate the probability that μ lies within any specified range about \bar{X} , as in Ex. S2, page 620. Results of such computations for various confidence levels are shown in Table S5.2, the use of which is illustrated in the following example.

Example S1. Three measurements give the weight of an object as 26.10, 26.28, 26.22 mg. If σ for a single measurement is 0.12 mg, give the interval within which μ lies, with a 95% probability of being correct.

$$\mu = \bar{X} \pm z(\sigma/\sqrt{N}) = 26.20 \pm 1.96(0.12/\sqrt{3}) = 26.20 \pm 0.14 \text{ mg}$$

z is chosen from Table S5.2, so that the range will include μ 95% of the time. Note that μ will lie outside this specified range 5% of the time. If greater certainty is desired, (1) the range must be extended, in which case the estimate becomes poorer, or (2) N must be increased, which entails more work.

In this example, the confidence level is 95%, the error probability is 5%, the 95% confidence interval is the 0.14 mg range about 26.20 mg from 26.06 to 26.34 mg, and the 95% confidence limits are 26.06 mg and 26.34 mg.

In practice, σ is usually not known, and the best estimate of precision is s , as calculated from the same single set of measurements as \bar{X} . In such a case, the estimate of precision is less certain than if σ is known, and a wider interval must be specified about \bar{X} to contain μ with the same degree of confidence. These intervals have been worked out by statisticians, and are given in Table S5.2 for various confidence levels. The following example illustrates further the use of Table S5.2.

Example S2. Assume that σ is not known for the three measurements of Ex. S1. Compute s , and state the 95% confidence interval.

$$s = \sqrt{\frac{(.10)^2 + (.08)^2 + (.02)^2}{3 - 1}} = 0.09 \text{ mg}$$

TABLE S5.2

LIMITS OF THE CONFIDENCE INTERVAL AROUND \bar{X} , WITHIN WHICH μ LIES

$$\mu = \bar{X} \pm z(\sigma/\sqrt{N}) \quad (\sigma \text{ known}) \quad \mu = \bar{X} \pm t(s/\sqrt{N}) \quad (\sigma \text{ unknown})$$

N, Number of Measurements in the Set from Which \bar{X} Is Computed	Confidence Level, or Per Cent Probability That μ Lies within the Stated Interval									
	80%		90%		95%		97.5%		99%	
	z	t	z	t	z	t	z	t	z	t
2	1.28	3.08	1.64	6.31	1.96	12.71	2.24	25.5	2.58	63.7
3		1.89		2.92		4.30		6.21		9.92
4		1.64		2.35		3.18		4.18		5.84
5		1.53		2.13		2.78		3.50		4.60
6		1.48		2.02		2.57		3.16		4.03
7		1.44		1.94		2.45		2.97		3.71
8		1.42		1.90		2.36		2.84		3.50
9		1.40		1.86		2.31		2.75		3.36
10		1.38		1.83		2.26		2.69		3.25
12		1.36		1.80		2.20		2.59		3.11
14		1.35		1.77		2.16		2.53		3.01
16		1.34		1.75		2.13		2.49		2.95
18		1.33		1.74		2.11		2.46		2.90
20		1.33		1.73		2.09		2.43		2.86
25		1.32		1.71		2.06		2.39		2.80
30		1.31		1.70		2.04		2.36		2.76
40		1.30		1.68		2.02		2.33		2.70
60		1.30		1.67		2.00		2.30		2.66
120		1.29		1.66		1.98		2.27		2.62
∞		1.28		1.64		1.96		2.24		2.58
	z	t	z	t	z	t	z	t	z	t
N	20%		10%		5%		2.5%		1%	
Error Probability, or Probability That μ Lies outside the Stated Interval										

$$\mu = \bar{X} \pm ts/\sqrt{N} = 26.20 \pm 4.30(0.09)/\sqrt{3} = 26.20 \pm 0.23 \text{ mg}$$

t is chosen from Table S5.2 so that the interval will include μ in 95% of the cases. The chances of being in error are 1:20.

Note that the t multipliers in Table S5.2 are larger than the corresponding z multipliers for small N , but that t approaches z as N becomes very large.

Comparison of \bar{X} with μ

In testing a method of analysis, a series of determinations may be

made on a sample whose true value is known. The observed \bar{X} is then compared with μ . If the absolute value of the difference $\bar{X} - \mu$ is greater than expected from the normal scattering of \bar{X} , then \bar{X} is judged to be significantly different from μ , and significant determinate error exists in the method.

The procedure for comparison again involves Table S5.2. The absolute difference $|\bar{X} - \mu|$ is compared with $z\sigma/\sqrt{N}$ if σ is known, or with ts/\sqrt{N} if σ is unknown, for the desired confidence level. If the observed $|\bar{X} - \mu|$ is greater than $z\sigma/\sqrt{N}$ or ts/\sqrt{N} , then \bar{X} and μ are too far apart to lie within the same confidence interval, and the conclusion may be drawn that \bar{X} and μ are *significantly different*, with the confidences stated in Table S5.2.

If, on the other hand, $|\bar{X} - \mu|$ is not greater than $z\sigma/\sqrt{N}$ or ts/\sqrt{N} , it may be concluded that there is no significant difference between \bar{X} and μ . The latter statement is emphatically not equivalent to saying that \bar{X} is equal to μ ; \bar{X} is "equal" to μ only within the rather wide limits of Table S5.2. \bar{X} and μ may therefore be quite different and still be judged not significantly different.

Sometimes \bar{X} and μ may differ considerably, but not sufficiently to be judged significantly different with good confidence. If the experimenter wishes to establish this smaller difference as significant, he must increase N or the precision of the method of measurement. It is not useful merely to lower the confidence level in an attempt to narrow the interval through which \bar{X} and μ are judged not significantly different, since this would also increase the chances of concluding erroneously that \bar{X} and μ are significantly different. In general, for small N , it is not considered reliable to use confidence levels below 90%. At the 90% confidence level, the error probability is 10%, and there is a 1:10 chance of judging \bar{X} and μ significantly different when in reality they are not. The 95% confidence level is used very frequently.

Example S1. Three measurements give the weight of an object as 26.10, 26.28, 26.22 mg. The true weight is 26.40 mg, and σ for a single measurement is 0.12 mg. (a) Is there a significant difference between \bar{X} and μ at the 95% confidence level? (b) What is the probability of the conclusion's being incorrect?

$$(a) |\bar{X} - \mu| = \left| \frac{26.10 + 26.28 + 26.22}{3} - 26.40 \right| = 0.20 \text{ mg}$$

At the 95% confidence level from Table S5.2,

$$z\sigma/\sqrt{N} = 1.96(0.12)/\sqrt{3} = 0.14 \text{ mg}$$

The conclusion is that \bar{X} is significantly different from μ , and that there is significant determinate error in the method of weighing.

(b) If $|\bar{X} - \mu|$ were 0.14 mg, the conclusion that \bar{X} is significantly different

from μ would have a 95% probability of being correct, and a 5% probability of being wrong.

Actually, $|\bar{X} - \mu|$ is greater than 0.14 mg, and the probability of the conclusion's being incorrect is less than 5%.

$$z = \frac{|\bar{X} - \mu|}{\sigma/\sqrt{N}} = \frac{0.20}{0.12/\sqrt{3}} = 2.9$$

which corresponds to a z value with an error probability of less than 1%. The probability of being incorrect in concluding that \bar{X} is significantly different from μ is therefore less than 1%.

Example S2. If σ is not given in Ex. S1, decide if there is a significant difference between \bar{X} and μ at the 95% confidence level.

$s = 0.09$ mg, calculated from the data of Ex. S1.

At the 95% confidence level from Table S5.2, $ts/\sqrt{N} = 4.30(0.09)/\sqrt{3} = 0.22$ mg, which is greater than $|\bar{X} - \mu| = 0.20$ mg; therefore the conclusion is that there is no significant difference between \bar{X} and μ .

Comparison of this conclusion with that of Ex. S1 shows that when σ is known, the resultant conclusions are more certain than when they are based upon s , which must be calculated from the single, small sample at hand.

The confidence levels and error probabilities of Table S5.2 apply when it is immaterial or unknown whether \bar{X} is greater or less than μ . To discover if \bar{X} is significantly greater than μ , or significantly less than μ , but not both, the error probabilities of Table S5.2 should be halved, and the confidence levels correspondingly increased. The reason for this is indicated in Ex. S2, page 620.

Example S3. It is suspected that a method of analysis for Al gives low results. Six determinations are made by the method on a reliable, homogeneous sample containing 27.73% Al. The value of \bar{X} is 27.53% Al, and s is 0.26% Al. Does the method give significantly low results at the 90% confidence level?

A 90% confidence level has an error probability of 10%. If we are interested in testing only if \bar{X} is significantly less than μ , Table S5.2 should be entered at an error probability of $2 \times 10\%$, or 20%.

$$ts/\sqrt{N} = 1.48(0.26)/\sqrt{6} = 0.16\% \text{ Al}$$

which is less than $|\bar{X} - \mu| = 0.20\%$. Hence \bar{X} is significantly lower than μ at the 90% confidence level.

The chances of this conclusion's being in error, and of there actually being no significant difference between \bar{X} and μ , are reckoned as follows:

$$\frac{|\bar{X} - \mu|}{s/\sqrt{N}} = \frac{0.20}{0.26/\sqrt{6}} = 1.88$$

This is a t value corresponding to an error probability between 10 and 20%, according to Table S5.2. Since we are testing only whether \bar{X} is less than μ , this error

probability should be halved. The chances of the foregoing conclusion's being incorrect are therefore between 5 and 10%, closer to 5%.

Comparison of Two Means

In checking a method of analysis, a mean, \bar{X}_a , of several determinations is often compared with another mean, \bar{X}_b , of several determinations arrived at by another method. If the absolute difference, $|\bar{X}_a - \bar{X}_b|$, is larger than can be explained by the random error of the means, it is concluded that the means are significantly different, and that the two methods of analysis give different results. The same sort of comparison must be made in judging whether there is a significant difference between two materials when analyzed by a certain method.

Let \bar{X}_a be one mean, composed of N_a determinations and having a standard deviation of σ_a for a single determination. Let \bar{X}_b be the other mean, composed of N_b determinations and having a standard deviation of σ_b for a single determination. Calculate σ_d of the difference of the two means,

$$\sigma_d = \sqrt{\sigma_{ma}^2 + \sigma_{mb}^2} = \sqrt{\frac{\sigma_a^2}{N_a} + \frac{\sigma_b^2}{N_b}}$$

From σ_d , calculate $z\sigma_d$, using the z value for any desired confidence level from Table S5.3. If the absolute difference, $|\bar{X}_a - \bar{X}_b|$, is greater than the value of $z\sigma_d$ selected for the desired confidence level, then \bar{X}_a and \bar{X}_b are judged significantly different. If, on the other hand, $|\bar{X}_a - \bar{X}_b|$ does not exceed $z\sigma_d$, then the two means are judged not significantly different, with the reservations already described on page 623.

Example S1. Five determinations by each of two methods on the Ca content of a very uniform material give the following results. *Method g*: 6.55, 6.51, 6.54, 6.57, 6.58% Ca. *Method h*: 6.55, 6.49, 6.53, 6.51, 6.52% Ca. For a single determination σ_g is 0.025% Ca, and σ_h is 0.020% Ca. Is there a significant difference between the two methods at the 90% confidence level?

$$\bar{X}_g = 6.55\% \text{ Ca}; \quad \bar{X}_h = 6.52\% \text{ Ca}; \quad |\bar{X}_g - \bar{X}_h| = 0.03\% \text{ Ca}$$

$$\sigma_d = \sqrt{\sigma_{mg}^2 + \sigma_{mh}^2} = \sqrt{(0.025)^2/5 + (0.020)^2/5} = 0.014\% \text{ Ca}$$

For the 90% confidence level, from Table S5.3, $z\sigma_d = 1.64(0.014) = 0.023\% \text{ Ca}$, which is less than the absolute difference between the two means. Hence there is a significant difference between the two means, and also between the two methods.

Example S2. What is the probability that the conclusion of Ex. S1 is incorrect?

If the observed difference between the two means had been 0.023% Ca, the conclusion above would have had a 90% probability of being correct, and a 10% prob-

TABLE S5.3

EXPECTED DIFFERENCE BETWEEN TWO MEANS, \bar{X}_a AND \bar{X}_b , FOR VARIOUS
CONFIDENCE LEVELS

$$|\bar{X}_a - \bar{X}_b| \leq z\sigma_d \quad (\sigma_a \text{ and } \sigma_b \text{ known})^*$$

$$|\bar{X}_a - \bar{X}_b| \leq t_{sp} \sqrt{1/(N_a) + 1/(N_b)} \quad (\sigma_a \text{ and } \sigma_b \text{ unknown})^*$$

$N_a + N_b$	Confidence Level, or Probability That $\bar{X}_a - \bar{X}_b$ Is Less Than the Limits above, When $\mu_a = \mu_b$									
	80%		90%		95%		97.5%		99%	
	z	t	z	t	z	t	z	t	z	t
3	1.28	3.08	1.64	6.31	1.96	12.71	2.24	25.5	2.58	63.7
4		1.89		2.92		4.30		6.21		9.92
5		1.64		2.35		3.18		4.18		5.84
6		1.53		2.13		2.78		3.50		4.60
7		1.48		2.01		2.57		3.16		4.03
8		1.44		1.94		2.45		2.97		3.71
9		1.42		1.90		2.36		2.84		3.50
10		1.40		1.86		2.31		2.75		3.36
12		1.37		1.81		2.23		2.63		3.17
14		1.36		1.78		2.18		2.56		3.06
16		1.35		1.76		2.14		2.51		2.98
18		1.34		1.75		2.12		2.47		2.92
20		1.33		1.73		2.10		2.45		2.88
25		1.32		1.71		2.07		2.40		2.81
30		1.31		1.70		2.05		2.37		2.76
40		1.30		1.69		2.02		2.34		2.71
60		1.30		1.67		2.00		2.30		2.66
120		1.29		1.66		1.98		2.27		2.62
∞		1.28		1.64		1.96		2.24		2.58
$N_a + N_b$	z	t	z	t	z	t	z	t	z	t
	20%		10%		5%		2.5%		1%	
	Error Probability, or Probability That $\bar{X}_a - \bar{X}_b$ Is Greater Than the Limits above, When $\mu_a = \mu_b$									

*See pp. 625 and 627 for definitions of σ_d and s_p .

ability of being incorrect. Actually, the observed difference is greater than 0.023% Ca, and the probability of the conclusion's being incorrect is less than 10%.

$$\frac{|\bar{X}_g - \bar{X}_h|}{\sigma_d} = \frac{0.03}{0.014} = 2.14$$

which corresponds to a z value with an error probability between 2.5 and 5%. The chances are between 2.5 and 5% that σ_g is equal to σ_h , and that the two methods are not significantly different.

In practice, σ_a and σ_b are often not known. In such a case, provided that it may be assumed that $\sigma_a = \sigma_b$, a weighted root-mean-square s has to be calculated. This s is called a "pooled" s by statisticians, is symbolized by s_p , and affords a better estimate of the precision than either s_a or s_b alone.

$$s_p = \sqrt{\frac{(N_a - 1)s_a^2 + (N_b - 1)s_b^2}{N_a + N_b - 2}}$$

If the observed absolute difference, $|\bar{X}_a - \bar{X}_b|$, is greater than the value $ts_p\sqrt{(1/N_a) + (1/N_b)}$, t being selected from Table S5.3 for the desired confidence level, then \bar{X}_a and \bar{X}_b are judged significantly different. If, on the other hand, $|\bar{X}_a - \bar{X}_b|$ does not exceed this critical value, \bar{X}_a and \bar{X}_b are judged not significantly different, with the reservations described on page 623.

This test is applicable only if $\sigma_a = \sigma_b$. If it is unknown whether or not $\sigma_a = \sigma_b$, there is no need to make this assumption blindly in order to test for a difference between two means by the method above. There is a test to determine if s_a and s_b differ significantly (p. 629). If this test shows no significant difference between s_a and s_b , they may be pooled. If this test does show a significant difference between s_a and s_b , then \bar{X}_a and \bar{X}_b must be compared by a procedure different from the one above (p. 635).

Example S3. If σ_g and σ_h are not given, is there a significant difference between the means of Ex. S1, at the 90% confidence level?

$$s_g = \sqrt{\frac{(.00)^2 + (.04)^2 + (.01)^2 + (.02)^2 + (.03)^2}{5 - 1}} = \sqrt{\frac{.0030}{4}}$$

$$s_h = \sqrt{\frac{(.03)^2 + (.03)^2 + (.01)^2 + (.01)^2 + (.00)^2}{5 - 1}} = \sqrt{\frac{.0020}{4}}$$

$$s_p = \sqrt{\frac{(5 - 1)(.0030)/4 + (5 - 1)(.0020)/4}{5 + 5 - 2}} = 0.025\% \text{ Ca}$$

From Table S5.3, for the 90% confidence level,

$$ts_p\sqrt{\frac{1}{N_g} + \frac{1}{N_h}} = 1.86(0.025)\sqrt{\frac{1}{5} + \frac{1}{5}} = 0.029\% \text{ Ca}$$

which is a trifle lower than the observed 0.03% difference, $|\bar{X}_g - \bar{X}_h|$. Hence there

is a significant difference between \bar{X}_a and \bar{X}_b . The probability of this conclusion's being incorrect is very close to 10% (1:10).

The confidence levels and error probabilities of Table S5.3 apply when it is immaterial or unknown whether \bar{X}_a is greater or less than \bar{X}_b . If it is desired to test whether one mean is significantly greater than the other, the error probabilities of Table S5.3 should be halved, and the corresponding confidence levels appropriately increased.

Example S4. Is \bar{X}_a in Ex. S1 significantly greater than \bar{X}_b at the 97.5% confidence level?

The 97.5% confidence level has an error probability of 2.5%. Since we are testing only whether \bar{X}_a is greater than \bar{X}_b , Table S5.3 should be entered at the 2(2.5) or 5% error probability.

$$z\sigma_d = 1.96(0.014) = 0.027\% \text{ Ca}$$

which is less than the difference $|\bar{X}_a - \bar{X}_b| = 0.03\% \text{ Ca}$. Hence \bar{X}_a is significantly greater than \bar{X}_b at the 97.5% confidence level. The chances of this statement's being in error are less than 2.5%.

Comparison of s with σ

It is occasionally necessary to discover if an observed s from a set of N determinations differs significantly from the known σ of the method of measurement. For example, such a comparison must be made if the experimenter wishes to test his own technique and equipment for a method of analysis known to have a certain σ . Table S5.1 (p. 617) is used in making this test. If the observed s^2/σ^2 falls within the limits of Table S5.1, then s and σ are judged not significantly different, with the reservations mentioned on page 623.

Example S1. An experimenter tests a method of analysis for Mg, using an unknown but homogeneous sample. Six determinations give 9.73, 9.82, 10.09, 9.62, 9.23, and 9.27% Mg. The method possesses a relative σ of 2.0% for a single determination. Is the worker's precision significantly poorer than the accepted precision?

$$\bar{X} = 9.63\% \text{ Mg}$$

$$s = 0.331\% \text{ Mg, or relative } s = \frac{0.331}{9.63} \times 100 = 3.43\%$$

$$\frac{s^2}{\sigma^2} = \frac{(3.43)^2}{(2.0)^2} = 2.94$$

If the experimenter really works with $\sigma = 2.0\%$, there is no significant difference between s and σ , and the chances of observing an s^2/σ^2 of 2.94 or higher for 6 determinations are only about 1%, from Table S5.1. It seems unwarranted to say that such an improbable event has occurred; it is more logical to say that s is significantly greater than σ and that the experimenter works with significantly poorer precision than is acceptable.

The chances of this decision's being incorrect (i.e., that s and σ are not significantly different) are about 1%.

Example S2. An analytical method has a relative σ of 2.0% for a single determination. A worker modifies the method in an attempt to improve the precision, and a test of the modification gives a relative s of 1.0%, as calculated from 4 determinations. Does the modification give significant improvement?

$$\frac{s^2}{\sigma^2} = \frac{(1.0)^2}{(2.0)^2} = 0.25$$

If there is no significant improvement, s is not significantly less than σ , and therefore, according to Table S5.1, the chances are 10% that s^2/σ^2 may have a value of 0.195 or lower. Hence the chances of observing an s^2/σ^2 of 0.25 or lower are greater than 10%, and the worker cannot confidently say that s is significantly less than σ .

The worker may still feel that the modification is an improvement, but he cannot prove this with certainty. If it is important not to reject the modification, more determinations must be made to give a more reliable estimate of the precision of the modified method.

Example S3. A change is made in a method of analysis having a relative σ of 0.12% for a single determination. Eight determinations by the modified method give an s of 0.20%. Does the modification produce a significant change in precision?

In this case it is immaterial (or perhaps cannot be predicted) whether the modification produces an increase or decrease of precision, so it is necessary to test s for being either significantly greater or less than σ .

From Table S5.1, for 8 determinations, if there is no significant difference between s and σ , the chances are 5% that s^2/σ^2 is less than 0.310 and 5% that s^2/σ^2 is greater than 2.01. Hence the chances are 90% that $0.310 \leq s^2/\sigma^2 \leq 2.01$.

The observed $s^2/\sigma^2 = (0.20)^2/(0.12)^2 = 2.8$. Hence there is a significant difference between s and σ .

The chances of this conclusion's being incorrect are less than 10%.

Comparison of Two s Values

It is sometimes necessary to decide whether or not an s_a observed from a set of N_a determinations is significantly different from an s_b observed from a set of N_b determinations, when the σ for neither set is known. Table S5.4 is used in this test, which is called the F test by statisticians. It is not necessary that \bar{X}_a be equal to \bar{X}_b .

If the ratio s_a^2/s_b^2 is greater than the tabled limits, it may be concluded that s_a is significantly greater than s_b , with the confidence levels shown. If, on the other hand, s_a^2/s_b^2 does not exceed the tabled limits, it may be concluded that s_a is not significantly greater than s_b , with the reservations given on page 623. Table S5.4 must be entered with three values: N_a , N_b , and the appropriate confidence level. Two different cases must be distinguished. (1) If it is known or postulated that one σ is greater than the other, the s corresponding to the larger σ should be placed in the numerator and called s_a . (2) If it is not known or postulated which σ is greater, the larger s should be called s_a and placed in the numerator, so that s_a^2/s_b^2 is always unity or greater. In this second

case the error probabilities of Table S5.4 should be doubled, and the corresponding confidence levels appropriately lowered.

TABLE S5.4

VALUES OF s_a^2/s_b^2 WHICH ARE EXCEEDED WITH PROBABILITIES OF 1, 2.5, 5, AND 10%, WHEN $\sigma_a = \sigma_b$ *

N_b	N_a										Error Probability (%)†	Confidence Level (%)‡
	2	3	4	5	6	8	10	15	20	∞		
2	39.9	49.5	53.6	55.8	57.2	58.9	60.0	61.1	61.6	63.3	10	90
	161	200	216	225	230	237	241	246	248	254	5	95
	648	800	864	900	922	948	963	982	992	1018	2.5	97.5
	4052	5000	5403	5625	5764	5928	6022	6140	6199	6366	1	99
3	8.53	9.00	9.16	9.24	9.29	9.35	9.38	9.42	9.44	9.49	10	90
	18.5	19.0	19.2	19.2	19.3	19.4	19.4	19.4	19.4	19.5	5	95
	38.5	39.0	39.2	39.2	39.3	39.4	39.4	39.4	39.4	39.5	2.5	97.5
	98.5	99.0	99.2	99.2	99.3	99.4	99.4	99.4	99.4	99.5	1	99
4	5.54	5.46	5.39	5.34	5.31	5.27	5.24	5.20	5.19	5.13	10	90
	10.1	9.55	9.28	9.12	9.01	8.89	8.81	8.71	8.67	8.53	5	95
	17.4	16.0	15.4	15.1	14.9	14.6	14.5	14.3	14.2	13.9	2.5	97.5
	34.1	30.8	29.5	28.7	28.2	27.7	27.3	26.9	26.7	26.1	1	99
5	4.54	4.32	4.19	4.11	4.05	3.98	3.94	3.88	3.85	3.76	10	90
	7.71	6.94	6.59	6.39	6.26	6.09	6.00	5.87	5.81	5.63	5	95
	12.2	10.6	9.98	9.60	9.36	9.07	8.90	8.69	8.58	8.26	2.5	97.5
	21.2	18.0	16.7	16.0	15.5	15.0	14.7	14.3	14.1	13.5	1	99
6	4.06	3.78	3.62	3.52	3.45	3.37	3.32	3.25	3.21	3.10	10	90
	6.61	5.79	5.41	5.19	5.05	4.88	4.77	4.64	4.57	4.36	5	95
	10.0	8.43	7.76	7.39	7.15	6.85	6.68	6.46	6.35	6.02	2.5	97.5
	16.3	13.3	12.1	11.4	11.0	10.5	10.2	9.77	9.59	9.02	1	99
8	3.59	3.26	3.07	2.96	2.88	2.78	2.72	2.64	2.60	2.47	10	90
	5.59	4.74	4.35	4.12	3.97	3.79	3.68	3.53	3.46	3.23	5	95
	8.07	6.54	5.89	5.52	5.29	4.99	4.82	4.60	4.49	4.14	2.5	97.5
	12.2	9.55	8.45	7.85	7.46	6.99	6.72	6.37	6.19	5.65	1	99
10	3.36	3.01	2.81	2.69	2.61	2.51	2.44	2.35	2.31	2.16	10	90
	5.12	4.26	3.86	3.63	3.48	3.29	3.18	3.03	2.95	2.71	5	95
	7.21	5.71	5.08	4.72	4.48	4.20	4.03	3.80	3.69	3.33	2.5	97.5
	10.6	8.02	6.99	6.42	6.06	5.61	5.35	5.01	4.84	4.31	1	99
15	3.10	2.73	2.52	2.39	2.31	2.19	2.12	2.02	1.97	1.80	10	90
	4.60	3.74	3.34	3.11	2.96	2.76	2.65	2.49	2.40	2.13	5	95
	6.30	4.86	4.24	3.89	3.66	3.38	3.21	2.98	2.86	2.49	2.5	97.5
	8.86	6.51	5.56	5.04	4.70	4.28	4.03	3.70	3.54	3.00	1	99
20	2.99	2.61	2.40	2.27	2.18	2.06	1.98	1.88	1.82	1.63	10	90
	4.38	3.52	3.13	2.90	2.74	2.54	2.42	2.26	2.17	1.88	5	95
	5.92	4.51	3.90	3.56	3.33	3.05	2.88	2.65	2.53	2.13	2.5	97.5
	8.18	5.93	5.01	4.50	4.17	3.77	3.52	3.20	3.03	2.49	1	99
∞	2.71	2.30	2.08	1.94	1.85	1.72	1.63	1.51	1.43	1.00	10	90
	3.84	3.00	2.60	2.37	2.21	2.01	1.88	1.69	1.59	1.00	5	95
	5.02	3.69	3.12	2.79	2.57	2.29	2.11	1.87	1.73	1.00	2.5	97.5
	6.63	4.61	3.78	3.32	3.02	2.64	2.41	2.08	1.91	1.00	1	99

* Data taken in part from the tables of E. S. Pearson, M. Merrington, and C. M. Thompson, *Biometrika*, 33, 73 (1943), with permission of the publisher.

† Error probability is the probability that s_a^2/s_b^2 will fall above the tabled values, when $\sigma_a = \sigma_b$.

‡ Confidence level is the probability that s_a^2/s_b^2 will fall below the tabled values, when $\sigma_a = \sigma_b$.

Inspection of Table S5.4 shows that when N_a and/or N_b are small, s_a and s_b must differ greatly before they may be judged significantly different with reasonable confidence. It should also be noted that when N_b becomes very large, s_b becomes an exact estimate of σ_b , and the critical values in Table S5.4 become the same as those in Table S5.1 (p. 617).

Example S1. Suppose that methods 1 and 2 are two different methods for measuring a quantity, and that both methods have the same σ . The following specific statements are made to interpret Table S5.4.

(a) Let there be measured an s_1 for method 1, using $N_1 = 5$, and an s_2 for method 2, using $N_2 = 10$. Then s_1^2/s_2^2 exceeds 2.69 10% of the time.

If an s_1^2/s_2^2 of 2.69 were observed, σ_1 would be judged significantly greater than σ_2 , at the 90% confidence level. This would be an erroneous conclusion, since both methods have the same σ . The chances of such an error's being committed are 10%.

Note, in addition, that s_2^2/s_1^2 exceeds 3.94 with a 10% probability. The reason for these two differing limits is the difference between N_1 and N_2 .

(b) Let there be measured an s_1 for method 1, using $N_1 = 6$, and an s_2 for method 2, using $N_2 = 6$. Then s_1^2/s_2^2 exceeds 7.15 with a 2.5% probability, and s_2^2/s_1^2 exceeds 7.15 with a 2.5% probability.

If we do not specify which s is placed in the numerator, but always place the larger s in the numerator, the chances that the observed ratio (s_1^2/s_2^2 or s_2^2/s_1^2 , whichever is greater than unity) will exceed 7.15 are just doubled to 5%. This is the reason for distinguishing the two cases mentioned in the text.

Example S2. Is the precision of method g significantly worse than that of method h in Ex. S1, page 625? Use the 90% confidence level, and assume that σ_g and σ_h are unknown.

The test is to find if σ_g is significantly greater than σ_h . Hence s_g should go in the numerator. There is a 10% probability that s_g^2/s_h^2 will exceed 4.11 (for $N_g = N_h = 5$), even if σ_g and σ_h are identical.

The observed $s_g^2/s_h^2 = 1.5$, from s_g and s_h as calculated in Ex. S3, page 627. Hence σ_g is not significantly greater than σ_h .

Example S3. For a set of 6 determinations, $s = 0.19$, and for another set of 15 determinations, $s = 0.39$. Are the precisions significantly different at the 90% confidence level?

Since it is not known which σ is the larger, the error probabilities of Table S5.4 are doubled, and the larger s is put in the numerator in making the test.

According to Table S5.4, for $N_a = 15$ and $N_b = 6$, there is a 10% probability that s_a^2/s_b^2 will exceed 4.64, if the larger s is arbitrarily chosen as s_a , and if $\sigma_a = \sigma_b$.

The observed $s_a^2/s_b^2 = (0.39)^2/(0.19)^2 = 4.22$. Hence s_a and s_b are not significantly different at the 90% confidence level.

Note that s_a and s_b are significantly different at the 80% confidence level. If it is said that σ_a and σ_b are significantly different, the chances of this statement's being incorrect are between 1:5 and 1:10.

Simplified Statistics, for $N \leq 10$

The median may be found after arranging the set in order of ascending value. The *median* is the middle value if N is odd, or the mean of the two middle values if N is even. The median possesses two advantages over the mean. First, the median may be computed more easily and rapidly than the mean, making it useful for quick statistical estimates. Second, it is not as sensitive to extreme values as the mean.

There is often a significant possibility that the extreme values in a set may contain determinate error, in which case the median may be used advantageously.

The median is a less efficient statistic than the mean, and gives a less reliable estimate of the true value. For $N \leq 10$, however, the loss in efficiency is small.

The range, w , may be found much more easily and rapidly than s . With the help of Table S5.5, w may be used to give a quick estimate of s . This estimate (s_w) may then be used to make the tests of significance that are described in the preceding sections.

The use of s_w estimated through w is sometimes defended on the grounds that the efficiency of s_w is only slightly inferior to the efficiency of s computed legitimately from squared deviations, provided that $N \leq 10$. This is not a safe argument, because w and therefore the estimate s_w are more sensitive to extreme values than s is. If there is any possibility of determinate error in the extreme values, the use of w and s_w is not recommended.

TABLE S5.5
ESTIMATION OF s FROM w ($s = Kw$)

	N								
	2	3	4	5	6	7	8	9	10
K	.886	.591	.486	.430	.395	.370	.351	.337	.325

Treatment of Discordant Data

Sometimes when several determinations are made on a single quantity, one result may differ considerably from the others of the group. The question then arises as to whether or not this determination should be rejected, for it may have a considerable effect on the mean. The following procedure is suggested for the interpretation of a small set of observations, if one observation is considerably different from the others.

1. The work leading to the discordant observation should be reexamined to see if some definite error might have been made in obtaining this measurement. If such an error is found, the observation should be rejected, no matter how it stands in relation to the other members of the set. This is the safest criterion for rejecting data, and seems to be the only one not open to question.

2. If no definite error may be associated with the discordant observation, additional determinations should be performed until a set of acceptable precision is obtained. Although this course is the ideally de-

sirable one, it is not always practical from the standpoint of time and effort.

3. If a result must be reported from the imprecise data at hand, it should be clearly recognized that the result has a good chance of being inaccurate. Either of two measures may be taken to reduce this inaccuracy, but neither guarantees success. For any particular set of data, one of these remedies may yield better results than the other, but there is no *a priori* way of selecting this one.

(a) Apply a statistical test to retain or reject the discordant value. Here the worker faces a dilemma. If he is too niggardly in rejecting data, erroneous values are not discarded and cause error in the mean. If the worker rejects data too freely, accurate values are discarded too often. Indiscriminate rejection of data is wasteful and deceptive; the reliability of the mean is decreased, and the precision of the work may be greatly overestimated, which may be very misleading in tracing sources of error. There are many tests for the rejection of discordant values.

One group of these tests accepts a rather low confidence that the discordant value be significantly different from the other members of the set. These tests reject passable data too indiscriminately, and they should never be used (B16).

Another group of tests demands a rather high confidence that the discordant member be significantly different from the remainder of the set. One of the simpler tests in this group is the *Q test* (D2). *Q* is the ratio of the difference between the discordant value and its nearest neighbor to the range. If *Q* exceeds the values in Table S5.6, the discordant value may be rejected with good (90%) confidence that it contains an error not present in other members of the set. The difficulty with the *Q test* is that it is too niggardly in rejecting data, especially when *N* is small. Application to specific cases shows that only grossly discordant values may be rejected.

Example. Four analyses on the percentage of Si in a sample give 0.21, 0.04, 0.25, 0.19. May the value 0.04% be rejected?

$$Q = \frac{0.19 - 0.04}{0.25 - 0.04} = \frac{0.15}{0.21} = 0.71$$

Q is less than the rejection quotient of 0.76 for 4 determinations, and the value of 0.04% Si cannot be rejected, even though it is intuitively suspect.

(b) Report the median of the set instead of the mean. The lower efficiency of the median is amply compensated by its insensitivity to the discordant value (p. 631).

TABLE S5.6
Q TEST FOR REJECTION OF DISCORDANT VALUES

	N							
	3	4	5	6	7	8	9	10
$Q_{.90}$.94	.76	.64	.56	.51	.47	.44	.41

Interpretation of Student Results

Suppose that a hypothetical class consists of three groups of 100 students each. The three groups differ only in the precision with which the students work. Let σ for a single determination be 0.10% for a Group I student, 0.20% for a Group II student, and 0.40% for a Group III student. Suppose, furthermore, that each student carries out triplicate determinations on a particular experiment, and reports the mean. The σ_m for the mean of three determinations is $0.10/\sqrt{3} = 0.058\%$ for a Group I student, $0.20/\sqrt{3} = 0.115\%$ for a Group II student, and $0.40/\sqrt{3} = 0.23\%$ for a Group III student.

Now suppose that grades are assigned on the basis of the error of each student's reported mean. A grade of A is given if the error is 0.1% or less, B if over 0.1% but not over 0.2%, C if over 0.2% but not over 0.4%, and D if over 0.4%. If no students make determinate errors, it may be seen from the table of areas (Appendix IIB) that 92% of the

TABLE S5.7
DISTRIBUTION OF ERRORS MADE BY STUDENTS IN VARIOUS PRECISION GROUPS*

PRECISION GROUP (σ)	GRADE GROUPS (ALLOWABLE ERROR OF MEAN)			
	A (below 0.1%)	B (0.1–0.2%)	C (0.2–0.4%)	D (over 0.4%)
I (0.1%).....	92	8	0	0
II (0.2%).....	62	30	8	0
III (0.4%).....	34	28	30	8

* Numbers in the table represent percentages of students in Groups I, II, and III falling in various error ranges or grade groups.

Group I students make errors less than 0.1% and fall in the A group, 8% make errors between 0.1 and 0.2% and fall in the B group, and practically none fall in the C or D groups. The distributions of students over the grade groups are summarized in Table S5.7.

It may be seen from the table that 8% of the Group I students are

classed as B students, even though in reality this 8% performs no worse than the other 92%, who are classed as A students. On the other hand, 62% of the Group II students are classed as A students, even though in reality they perform no better than the remaining 38% of Group II students in the B- and C-grade groups, and even though in reality they actually work with poorer precision than the 8% of Group I students in the B class. These discrepancies arise purely from chance, and are not due to inequalities in the individual students.

Further examination of Table S5.7 confirms that there is considerable inequity in grading. The conclusion which must be drawn is that there can be no fine grading on the basis of triplicate determinations for one experiment alone. Other grading systems which might be devised suffer similar disadvantages.

This does not mean that the grading situation is hopeless, for, when the results of many experiments are averaged over the semester, definite conclusions may be drawn. Thus it may be seen that a Group I student would have only a small proportion of B and C experiments, whereas the experiments of a Group III student would be fairly evenly distributed over A, B, and C grades.

It is important for the student to understand this situation, and to interpret the grades on his experiments as follows: (1) A good grade on a single experiment should be regarded as only indicative that the student is working with good accuracy. Only when a student receives good grades over several experiments can he be fairly certain that he is working in this category. (2) Experiments on which poor grades are received are the ones that deserve the student's attention. A poor grade indicates either that the precision is not acceptable, or that determinate errors have been made. In either case a careful assessment of the work is necessary, and the sources of error should be sought before the next experiment is begun, so that such error will not be repeated. (3) Perfect performance is not expected of any student. Every student occasionally obtains an s that is several times larger than his characteristic σ . This must be allowed for in the final grading.

More General Statistical Tests

The preceding tests are elementary, designed to compare two means or two s values, and, though they cover many experimental situations, they are of limited application. There are more general tests which allow comparison of more than two means and of more than two s values. Such methods are beyond the scope of this book, but may be found in elementary statistics texts (D8).

LIMITATIONS ON THE USE OF CORRECTIONS

(See Sec. 5E.3f, p. 51)

For any correction to be valid, the conditions under which it is determined must be identical with the conditions of the analysis to be corrected. However, by definition, the error that requires the correction is due to variables which cannot be entirely controlled, or which may even be unknown. Not only may these variables change suddenly, but there may be no noticeable indication of the change, even after it has occurred. For these reasons, corrections are seldom accurately determinable, and they must be checked and redetermined frequently.

One of the most troublesome sources of variation in the magnitude of errors is due to interfering substances in the sample. Such interferences may totally invalidate any corrections determined in the absence of the interferences. Whenever such interferences are suspected, several procedures may be used to apply corrections. A few typical ones are given below.

(1) The interferences may be removed. This is the most desirable method, but it may be experimentally troublesome. (2) A synthetic mixture that contains a known amount of the sought-for substance in the presence of the same kinds and amounts of interferences as are suspected in the unknown is made up and analyzed as a control. This requires information that is seldom available. (3) The method of *standard addition* may be used. Here the result given by the unknown sample is compared with that given by the same-sized unknown sample to which has been added a known amount of sought-for substance as a control. These values are substituted into Eq. 5.10 (p. 50) to determine the amount of sought-for substance in the unknown sample alone.

$$\frac{(\text{Weight of } X \text{ in unknown sample})}{(\text{Weight of } X \text{ in unknown sample} + \text{weight of } X \text{ added})} = \frac{(\text{result on unknown sample alone})}{(\text{result on unknown sample with added } X)}$$

This procedure must be used carefully, however, since only proportional error is compensated. Constant error is not eliminated.

CHECKING THE ACCURACY OF ANALYTICAL PROCEDURES OR RESULTS

(See Sec. 5G, p. 53)

Use of another method of analysis. Perhaps the most reliable and certain way of checking the accuracy of a method is to analyze the same sample by another, independent, accepted method. Several determinations should be performed by each method, so that good estimates of the precision of each method may be obtained. If there is a significant

difference between the two means obtained, determinate error is probably present in one or both methods. Although the magnitude and the sign of the discrepancy between the two means may indicate the nature of the error, further work must usually be done to discover its source.

If there is no significant difference between the two means, there is no reason to suspect the presence of appreciable determinate error in either method. (This statement assumes that determinate error, if present, is unlikely to be identical for both methods of analysis.) In such a case, the (random) error of each method is measured by its s .

Because the sample is analyzed by two different methods, this checking procedure is particularly useful for determining the applicability of an analytical method to a particular kind of sample. This would be especially important if interferences that might invalidate the method were suspected to be present. However, for an all-round check of method, facilities, and personnel, this procedure is generally not desirable because of the time, effort, and expense required to set up for another method of analysis. This checking procedure is also worthless for revealing sources of determinate error that affect both analytical methods to the same extent.

Use of standard samples. It is often possible to obtain known or analyzed samples containing a sought-for constituent. Many reagent-grade chemicals are obtainable in pure form, and may be used as standard samples containing known percentages of the constituent elements. Through the National Bureau of Standards, complex mixtures containing known amounts of certain components are available at nominal prices. For example, there are steels containing known amounts of C, P, S, Si, Mn, Cu, Ni, V, As, Sn, and other elements. Analyzed samples of other ferrous and nonferrous alloys, ores, and ceramic materials are also available. A useful list of hundreds of such samples, with representative analyses on each, may be obtained from the Bureau (U4). The American Society for Testing and Materials also describes specifications on many industrial and natural materials (A11).

To check the accuracy of a method of analysis, several determinations are made on a standard sample that contains a known amount of the sought-for substance. A reliable estimate of the precision (s) of the method may thus be obtained. If there is a significant difference between the observed and known amounts, determinate error probably exists in the method. If there is no significant difference between the observed and known amounts, s is taken as a measure of the method's random error.

The analysis of standard or known samples is a common and adequate general check on the accuracy of analytical methods, facilities, and personnel. The effort of such a check is no greater than that required

for analysis of a single unknown sample. It must be cautioned, however, that this checking procedure is valueless if the nature of the sample is suspect or unknown. For example, analyses of iron ore samples, which may or may not contain interferences, cannot be checked with samples of pure Fe_2O_3 . The check must be run using standard samples as similar to the ore samples as possible. If such samples cannot be obtained or prepared, the comparison is not valid.

Attainment of acceptable precision. If it is known with certainty that determinate error is absent, s may be taken as a measure of the random error of the set of measurements. In routine analyses (i.e., analyses performed by an experienced analyst, with proved equipment and an accepted method) only occasional and accidental errors occur to decrease precision. Most analyses are routine, and in such cases acceptable precision is taken as an indication of acceptable accuracy. This checking procedure is the one most frequently used. However, it is also the most unreliable, for it does not reveal determinate errors but only accidental or gross errors.

Attainment of a material or ionic balance. Once in a great while complete analyses are performed for all constituents in a sample. In such analyses the percentages of all constituents should sum to 100%. If the sum is less than 100% by an amount greater than is warranted by the precision with which the constituents are determined, then not all constituents have been found, or the percentage of one or more of the constituents is erroneously low. If the sum is significantly greater than 100%, then the percentage of one or more of the constituents is erroneously high.

Because the uncertainty of the sum is of the same order of magnitude as the uncertainty of the major constituents, this procedure is not accurate for checking minor constituents, and may not even reveal whether or not they have all been found. Also, a summation equal to 100% does not definitely prove that all the constituent analyses are correct, for two or more errors may compensate one another. The chances of such compensation are not so slim as might at first be thought. In some schemes of analysis, for instance, the lost part of one constituent is sometimes recovered and included with a subsequently separated constituent. Thus fulfillment of the material balance does not guarantee complete accuracy.

In the analysis of solutions, the sum of the equivalents of cation constituents must be equal to the sum of the equivalents of the anion constituents. If all constituents are determined, this ionic balance may be used to check the accuracy in the same way as the mass summation described above.

This checking procedure is seldom used, because complete analyses

for all constituents are seldom performed. In fact, the material or ionic balance is more often used to determine the amount of a major constituent by difference, in order to save the time that would be required for a direct analysis of that constituent.

COMPUTATION

Additional Computation Rules

(See Sec. 5H.3, p. 56)

Rule 5. All factors should be rounded before computation. In rounding intermediate factors, one more digit is generally retained than is necessary, and only the final answer is rounded to the required uncertainty. This saves time in computation.

Examples

(a)

$$\begin{array}{r} 1.02345 \\ 21.1 \\ \underline{2.1002} \\ 24.22 \end{array}$$

(b)

$$\frac{1.012345 \times 27.3}{9} = 3.03$$

↑
↑

1 in 10.
Round answer so that its uncertainty lies between 1 in 5 and 1 in 50.

Rule 6. Occasionally a result is obtained through several stepwise calculations. If the foregoing rules are applied indiscriminately to each step, an accumulation of spurious digits may occur. It must be remembered that the final result can be no more precise than the least precise component of the original data from which that result is calculated.

Rule 7. The log of a number should have as many digits to the right of the decimal as there are significant digits in the number.

Examples

(a)

$$\log 1.23 = 0.090$$

(b)

$$\log 123 = 2.090$$

(c)

$$\log 0.000012345 = 0.09150 - 5 = -4.90850$$

Rule 8. Generally, a mean has the same number of significant digits as the observations upon which it is based. (More precisely, such a number of significant digits should be retained that the uncertainty of the mean corresponds approximately to its standard deviation.)

Example. If a mean is composed of many determinations, and if these lie close together, so that s is small, it may be statistically justifiable to retain one more digit in the mean than appears in the individual determinations. Suppose that ten measurements on the length of an object give 10.21, 10.22, 10.21, 10.22, 10.21, 10.21, 10.22, 10.20, 10.21, and 10.21 cm. It is perfectly justifiable to express the mean as 10.212 cm, since s/\sqrt{N} is only 0.002 cm.

If an uncontrolled and varying quantity is measured with spurious precision, it may be desirable to drop digits from the mean. Suppose that hourly measurements of the temperature of a poorly controlled water bath give 24.00, 24.32, 24.50, 24.96, 25.12, 23.91, 25.63, 23.81, 24.38, and 24.97°C. It is quite pointless to express the mean as 24.56°C, since s/\sqrt{N} is 0.2°C. A mean of 24.6°C is more realistic.

The Error of a Computed Result

(See Sec. 5H.4, p. 57)

The error of a simple computed result. Benedetti-Pichler (B8) has summarized methods of estimating the error of a computed result from the errors of the component factors, for the special cases where the result is obtained by (1) addition and/or subtraction, or (2) multiplication and/or division, as shown in Table S5.8.

TABLE S5.8
ERROR OF A COMPUTED RESULT*

R = computed result.

X, Y, Z = experimental quantities from which R is computed.

r, x, y, z = absolute errors or absolute σ 's of R, X, Y, Z , respectively.

$\frac{r}{R}, \frac{x}{X}, \frac{y}{Y}, \frac{z}{Z}$ = relative errors or relative σ 's of R, X, Y, Z , respectively.

ERROR OF R	OPERATION	
	R Calculated as a Sum or Difference, $R = X + Y - Z$	R Calculated as a Product or Quotient, $R = XY/Z$
Determinate	$r = x + y - z$ (a)	$\frac{r}{R} = \frac{x}{X} + \frac{y}{Y} - \frac{z}{Z}$ (b)
Random	$r = \sqrt{x^2 + y^2 + z^2}$ (c)	$\frac{r}{R} = \sqrt{\left(\frac{x}{X}\right)^2 + \left(\frac{y}{Y}\right)^2 + \left(\frac{z}{Z}\right)^2}$ (d)

* Reprinted from A. A. Benedetti-Pichler, *Industrial and Engineering Chemistry, Analytical Edition*, 8, 373 (1936), Table 4, by permission of the publisher.

The calculation of the error depends upon whether it is determinate or random. If the component errors are determinate, the error of the result is a well-defined quantity, depending only upon the errors of the component quantities. If the errors of the components are random, the

error of the result is best expressed by its standard deviation (σ); the actual error varies from one measurement to the next, being distributed about an error of zero with the standard deviation calculated as in Table S5.8.

Where a result is obtained simply by addition and/or subtraction, or by multiplication and/or division, the equations in the table are directly applicable. Where a result is obtained by both additive and multiplicative operations, the error of the result is obtained by applying the equations of Table S5.8 in steps, as shown in the following illustrative examples. These methods of estimating the error of a computed result cover most of the calculations of elementary analytical chemistry.

Example S1. The relative error in the weight of a sample is $+0.2\%$, and that in the weight of a sought-for constituent is $+0.3\%$. What is the relative error in the percentage of sought-for constituent in the sample?

$$\% \text{ of sought-for constituent} = 100(\text{wt. constituent})/(\text{wt. sample})$$

Since the errors are determinate, the relative determinate error in the percentage of sought-for constituent is $0.3\% - 0.2\%$, or 0.1% , according to Eq. b, Table S5.8.

Example S2. The σ of the weight of a 10-g object is 0.0002 g. What are the absolute σ and relative σ of the sum of the weights of ten such objects?

Since errors are random, the absolute σ of the sum of ten weights is, from Eq. c,

$$\sqrt{10(0.0002)^2} = 0.0006 \text{ g}$$

Therefore the relative σ of the sum of ten weights is

$$\frac{0.0006}{100} = 0.000006, \text{ or } 0.0006\%$$

Example S3. A result, R , is calculated as $R = (X + Y + Z)T/UV$. The absolute σ 's of T , U , V , X , Y , and Z are t , u , v , x , y , and z , respectively.

(a) Calculate the relative σ of R .

The absolute σ of the sum, $(X + Y + Z)$, is

$$\sqrt{x^2 + y^2 + z^2}$$

The relative σ of the sum, $(X + Y + Z)$, is

$$\frac{\sqrt{x^2 + y^2 + z^2}}{X + Y + Z}$$

Therefore the relative σ of R , from Eq. d, is

$$\sqrt{\frac{x^2 + y^2 + z^2}{(X + Y + Z)^2} + \left(\frac{t}{T}\right)^2 + \left(\frac{u}{U}\right)^2 + \left(\frac{v}{V}\right)^2}$$

(b) If X , Y , Z , and T are 10 g each, and U and V are 5 g each, what are the absolute σ and relative σ of R ? Assume that the absolute σ of each weight is 0.0001 g.

From part *a*, the relative σ of R is

$$\sqrt{\frac{3(0.0001)^2}{(30)^2} + \left(\frac{0.0001}{10}\right)^2 + 2\left(\frac{0.0001}{5}\right)^2} = 3 \times 10^{-5}$$

Hence the absolute σ of R is

$$3 \times 10^{-5} \times \frac{30 \times 10}{5 \times 5} \text{ or } 0.0004 \text{ g}$$

The error of any computed result. In computations involving more complicated functions (i.e., logarithmic, trigonometric, etc.), the equations of Table S5.8 are inadequate, and the errors must be calculated specifically for the cases at hand. The general methods for estimating the error in any computed result are outlined in this section.

Let R be a result computed as a function of the independent variables, X, Y, \dots ,

$$R = f(X, Y, \dots) \quad (\text{Sa})$$

Also, let r, x, y, \dots be the absolute errors (if determinate) or absolute standard deviations (if random) in these variables. The relative errors or relative σ 's are then $r/R, x/X, y/Y, \dots$, in accord with the nomenclature of Table S5.8.

If the errors are determinate,

$$r = \frac{\partial R}{\partial X} x + \frac{\partial R}{\partial Y} y + \dots \quad (\text{Sb})$$

If the errors are random,

$$r^2 = \left(\frac{\partial R}{\partial X}\right)^2 x^2 + \left(\frac{\partial R}{\partial Y}\right)^2 y^2 + \dots \quad (\text{Sc})$$

The derivation of Eqs. *Sb* and *Sc* may be found in many mathematics texts (C12). It is their application that is of interest to the analytical chemist, as illustrated in the following examples. The differentiation processes required in most applications are not difficult.

Example S1. The equations of Table S5.8 may be derived from Eqs. *Sb* and *Sc* above. As an example:

If $R = XY/Z$, then for random error, according to Eq. *Sc*,

$$r^2 = (Y/Z)^2 x^2 + (X/Z)^2 y^2 + (-XY/Z^2)^2 z^2$$

Dividing the left side of this equation by R^2 and the right side by the equal quantity $(XY/Z)^2$ does not destroy the equality, and gives Eq. *d* of Table S5.8.

Example S2. The relation between the pH of a solution and the hydrogen-ion molarity, C , is $pH = -\log_{10} C$. Calculate the error in pH due to a relative error of 1.0% in C .

$$\begin{aligned}
 \left(\frac{\text{Determinate}}{\text{error in } pH} \right) &= \frac{\partial}{\partial C} (-\log_{10} C) \times \left(\frac{\text{absolute}}{\text{error in } C} \right) \quad (\text{From Eq. Sb}) \\
 &= \frac{-\log_{10} e}{C} \times \left(\frac{\text{absolute}}{\text{error in } C} \right) \\
 &= -\log_{10} e \times \left(\frac{\text{relative}}{\text{error in } C} \right) \\
 &= (-0.43)(0.010) = -0.0043 \text{ pH units}
 \end{aligned}$$

Computational Short Cuts and Approximations

Quite often, it is necessary to manipulate numbers that are rather close to unity, but that have many significant figures. For example, $1.00276/0.99865$. The slide rule cannot be used directly for such computations. Although logs or longhand may be used, the time of computation is shortened (and chances of error decreased) by taking advantage of the methods and approximations below. With a little practice, these methods are very rapid.

To multiply a number by another number close to unity:

$$\begin{aligned}
 26.023 \times 1.0076 &= 26.023(1.00 \cdots + 0.0076) \\
 &= 26.023 + 26.023(0.0076) = 26.221
 \end{aligned}$$

↑ Calculate with slide rule, to give 0.198.

$$\text{Generalization:} \quad a(1 \pm x) = a \pm ax \quad (\text{Sa})$$

To divide a number by another number close to unity:

$$\begin{aligned}
 \frac{76.023}{1.00147} &= \frac{76.023}{1.00 \cdots + 0.00147} \times \frac{1.00 \cdots - 0.00147}{1.00 \cdots - 0.00147} \\
 &= \frac{76.023 - 76.023(0.00147)}{1.00 \cdots - (0.00147)^2} \leftarrow \begin{array}{l} \text{Use slide rule, to give 0.112.} \\ \text{Negligible, around } 10^{-6}. \end{array} \\
 &= 76.023 - 0.112 = 75.911
 \end{aligned}$$

Generalization:

$$\frac{a}{1 \pm x} = a(1 \mp x) = a \mp ax \quad (x \ll 1) \quad (\text{Sb})$$

To divide two numbers close to each other:

$$\frac{25.997}{26.010} = \frac{26.010 - 0.013}{26.010} = 1.00\cdots - \frac{0.013}{26.010} \leftarrow \begin{array}{l} \text{Use slide} \\ \text{rule, to give} \\ 0.00050. \end{array}$$

$$= 1.00\cdots - 0.00050 = 0.99950$$

To obtain the n th power of a number close to unity:

$$(1.0025)^2 = (1.00\cdots + 0.0025)^2 = 1.00\cdots + 2(0.0025) + (0.0025)^2$$

$$= 1.00\cdots + 0.0050 + \text{negligible term} = 1.0050$$

$$\text{Generalization: } (1 \pm x)^n = 1 \pm nx \quad (x \ll 1) \quad (\text{Sc})$$

To obtain the n th root of a number close to unity:

Use Eq. Sc conversely, which gives

$$\sqrt[n]{1 \pm x} = 1 \pm \frac{x}{n} \quad (x \ll 1) \quad (\text{Sd})$$

Thus

$$\sqrt{1.00924} = \sqrt{1.00\cdots + 0.00924}$$

$$= 1.00\cdots + \frac{0.00924}{2} = 1.00462$$

SUPPLEMENTARY QUESTIONS

Section 5C

S1. What is the advantage of expressing errors in σ units?

S2. What is wrong with the following statements? (a) As calculated from 4 measurements, σ is 0.15 cm. (b) Out of 10 determinations, 9 will fall within 1.645σ of the mean.

S3. Explain why the concept of the confidence interval is important.

S4. Define and contrast a confidence level with a confidence interval. What is meant by saying that the 90% confidence interval of a quantity is 19.65 cm to 20.23 cm?

S5. The statistical test described on page 623 can prove a difference between \bar{X} and μ with good confidence, but cannot prove the identity of \bar{X} and μ with good confidence. Explain.

S6. Why are the t values greater than z values for corresponding confidence levels?

S7. In testing for a difference between \bar{X} and μ , the error probability could be decreased by working at very high confidence levels, say, 99% or higher. What is the disadvantage of doing this?

S8. For any method performed by you in the laboratory, list approximately a dozen specific errors. Classify these into a table of three columns (according to source) and two rows (random or determinate). For the determinate errors, speculate as to what kind each might be.

Sections 5E-G

S1. An observed error is reproducible, but is a mixture of constant and propor-

tional error. Outline briefly, but specifically, several different ways of correcting and/or compensating for the error.

S2. Summarize in tabular form the important characteristics of the four methods for checking the accuracy of an analytical procedure or result, paying particular attention to the principal uses and reliability of each method.

Section 5H

S1. It is easy to explain Eq. *a* in Table S5.8 (p. 640), for it is a matter of common sense that the error of a sum should be the sum of the errors of the component quantities, if these errors are determinate. Explain why the random error (i.e., σ) of a sum would most likely be less than the sum of the random errors of the component quantities, in accord with Eq. *c*.

S2. With the use of log tables, show that Rule 7 (p. 639) for the number of significant digits in the log of a quantity applies in several randomly chosen cases.

SUPPLEMENTARY PROBLEMS

Section 5C

S1. From the equation of the normal curve, calculate the relative probabilities of occurrence for errors of the following magnitudes: 0, σ , $-\sigma$, 1.64σ , 2σ , 5σ . (Assume unity for the occurrence of zero error.) Compare answers with Appendix IIA (p. 908).

S2. Use the table of areas in Appendix IIB (p. 909) to estimate the probability that an observed X will fall (a) outside the range $\mu \pm 2\sigma$, (b) above the limit $\mu + 2\sigma$. Compare answers with the confidence levels given in Table S5.2 (p. 622).

Ans. (a) 2×0.02275 ; (b) 0.02275.

S3. Examination of a large number of determinations with a particular weighing method shows that 82.5% fall within 1.8 mg of the true value. What is σ for the method?

Ans. 1.3 mg.

S4. For a method of copper analysis, σ is 0.22% Cu. What is the probability that the error of a determination will exceed 0.50% Cu?

S5. For a certain method of measurement, $\sigma = 0.30$ cm. Give the 95% confidence limits for s as determined from a set of 5 determinations. *Ans.* 0.104–0.50 cm.

S6. For a certain method of measurement, $s = 0.55$ cm, as calculated from 8 determinations. Give the 98% confidence limits for σ .

S7. For a single determination, $\sigma = 0.40$ cm. What is the σ for a mean of 6 determinations? Over what range of length would \bar{X} for 6 determinations be expected to fall 95% of the time?

Ans. 0.16 cm; 0.64 cm.

S8. Draw the distribution curve for s^2/σ^2 onto Fig. S5.2 (p. 616) when $N = \infty$. Interpret this curve.

S9. For a single observation, $\sigma = 0.01$ cm. How many measurements would be required to report a mean with a $\sigma_m = 0.001$ cm? *Ans.* 100.

S10. A worker intends to make replicate determinations on a sample, using a particular method of zinc analysis ($\sigma = 0.12\%$ Zn). How many determinations must constitute his mean if he wishes to be 99% sure that it will fall within 0.10% of the true value?

S11. For a certain method of analysis, σ is 0.045% Pb. Seven replicate determinations on a sample give an average value of 56.25% Pb. What is the probability that this mean falls within 0.05% Pb of the true value? That is, how confident can one be that the mean is within 0.05% Pb of the true value? *Ans.* 99.7%.

S12. Using all 80 measurements of Prob. 3, Secs. 5B-G (p. 60), give the 90% confidence limits for μ and σ .

S13. Using the table of areas (Appendix IIB), derive the z value of 1.64 for the 90% confidence level of Table S5.2.

S14. For a certain method of measurement, $\sigma = 0.5$ cm, and the average of 5 determinations on a length is 1803.2 cm. Give the 90% confidence limits for μ .

S15. Three measurements of the weight of an object give 27.1, 27.5, and 27.6 mg. What are the 90 and 99% confidence limits for the true weight?

Ans. 27.4 ± 0.4 mg, 27.4 ± 1.5 mg.

S16. If one is satisfied with a prediction on the 90% confidence level, can it be concluded that there is a significant difference between \bar{X} and μ in Ex. S2, page 624?

S17. After concluding that there is no significant difference between \bar{X} and μ in Ex. S2, page 624, the investigator makes a second set of 3 more measurements and obtains 26.20, 26.30, and 26.10 mg. May he conclude that there is a significant difference between \bar{X} (of the 6 measurements) and μ at the 95% confidence level? Discuss the answer in view of the fact that the means of the two sets are identical.

Ans. Yes.

S18. The average percentage of Mo in a sample was found to be 27.21% Mo when analyzed by 15 students in a class, with $s = 0.03\%$ Mo. Another class of 12 students obtained 27.18% Mo, with the same standard deviation. Is there a significant difference between the two classes?

S19. Seven determinations of the percentage of Cu in a sample give 39.3, 41.2, 40.4, 40.0, 41.1, 39.9, and 40.9% Cu.

(a) Compute \bar{X} and s .

Ans. 40.4% Cu, 0.7% Cu.

(b) Give the 95% confidence limits for μ and σ .

Ans. $40.4 \pm 0.7\%$ Cu, 0.5 to 1.6% Cu.

S20. The sample of Prob. S19 contains 39.5% Cu, and σ is 0.35% Cu. Is \bar{X} significantly different from μ , and is s significantly larger than σ , at the 90% confidence level?

S21. The sample of Prob. S19 is analyzed by a second method, which gives 39.6, 40.0, 40.3, 39.7, 39.2, and 39.4% Cu.

(a) Are the means or s values of the two methods significantly different at the 95% confidence level?

(b) Is \bar{X} or s for the method of Prob. S19 significantly larger than \bar{X} or s for the second method at the 95% confidence level?

Ans. (a) No; (b) for the method of Prob. S19, \bar{X} is significantly greater, but s is not.

S22. Lord Rayleigh prepared nitrogen samples by several different methods. The density of each sample was measured as the weight of gas required to fill a particular flask at a certain temperature and a certain pressure. Weights of nitrogen samples prepared by decomposition of various nitrogen compounds were 2.29890, 2.29940, 2.29849, 2.30054 g. Weights of "nitrogen" prepared by removing oxygen from air in various ways were 2.31001, 2.31163, 2.31028 g. Is the density of nitrogen prepared from nitrogen compounds significantly different from that prepared from air? What are the chances of the conclusion being in error? Study of this difference led to the discovery of the inert gases by Sir William Ramsey (C12).

S23. In testing a certain method of weighing, 76.23% of a large number of measurements fall within 0.49 mg of the true value. A new worker uses the method to obtain 4 weights on an object as 26.1112, 26.1102, 26.1123, 26.1115 g. Calculate σ for the method and s for the worker. Is s significantly larger than σ , at the 90% confidence level?

Ans. $\sigma = 0.41$ mg; $s = 0.87$ mg; yes.

S24. Estimate values of s_w from w for the data of Probs. 1-4, Sec. 5A (p. 59), and

compare with the corresponding values of s calculated legitimately from squared deviations.

S25. Apply the Q test to the extreme values of Probs. 1–4, Sec. 5A.

Ans. No values may be rejected.

S26. Two analyses on the percentage of Sr in a sample give 0.27 and 0.29% Sr.

(a) How low would a third value have to be, in order to reject it with 90% confidence?

(b) How high would a third value have to be, in order to reject it with 90% confidence?

(c) Comment on the usefulness of the Q test for a small number of determinations.

S27. There is a rule (the “4d” rule) which states that a discordant value may be rejected if its deviation from the mean of the rest of the values is more than four times the average deviation of the rest of the values. Apply this rule to the set 27.7, 27.1, 27.4, 28.3% Be, and compare the decision with the decision obtained with the Q test.

Ans. Reject 28.3% Be by “4d” rule, but not by Q test.

Section 5E

S1. In the method of standard addition, an unknown sample requires 22.19 ml of standard solution for titration. The same amount of unknown sample plus 0.0470 g of the pure sought-for substance requires 48.20 ml of the standard solution for titration. What is the weight of sought-for substance in the sample? *Ans.* 0.0401 g.

S2. (a) In the determination of Al with reagent-grade NH_3 (Table 5.1, p. 47), assume (incorrectly) that the error is proportional. With the 4-g alum sample as a control, calculate the weight of Al_2O_3 in the sample that gives 0.1288 g of precipitate. Compare the calculated and correct weights. (b) Draw a correction curve for the determination with reagent-grade NH_3 , using the data in Table 5.1. The residual errors in the foregoing inadequate compensation procedure may be seen from the plot if a straight line is drawn from the control through the origin. The line represents the corrections automatically made with the control procedure, which assumes the error to be proportional. It may be seen that the residual errors of the control method are small for sample sizes close to the control, but are very large for sample sizes greatly different from the control.

Section 5G

S1. Seven determinations for Sn by a method under test on a sample known to contain 21.90% Sn gave 21.9, 20.9, 20.7, 23.1, 24.2, 22.4, 20.6% Sn. Calculate s for a single determination. Is \bar{X} significantly different from μ at the 90% confidence level? Describe the nature of the error.

Ans. 1.4% Sn; no; predominantly random.

S2. Repeat Prob. S1 for the following results: 21.9, 21.8, 21.7, 22.1, 22.0, 21.9% Sn.

S3. Repeat Prob. S1 for the following results: 22.9, 21.9, 22.4, 22.7, 23.1% Sn.

Ans. 0.47% Sn; yes; predominantly determinate.

S4. To test a sampling method, two samples were taken from the same batch of material and analyzed for substance Y by the same procedure. Analyses on sample 1 gave 50.7, 50.8, 50.2, and 50.5% Y; analyses on sample 2 gave 50.2, 50.4, and 50.3% Y. Is there a significant difference between the two samples at the 90% confidence level?

S5. Analysis of a sample for CO_2 by a new method gave 42.1, 42.9, 42.7, and 42.3%. Analysis of the same sample by another accepted method gave 42.5, 42.5, 42.7, and 42.7%. Is there any significant difference between the two methods?

Ans. At the 90% confidence level, neither the s 's nor the \bar{X} 's differ significantly.

S6. Identical samples are given to analysts A and B in order that their techniques may be compared. Analyst A reports 49.84, 49.87, and 49.87%, and analyst B reports 49.91, 49.87, 49.93, and 49.92%, of the sought-for constituent. Discuss the differences between the analysts, if any.

S7. A sample is analyzed for four components, W, X, Y, and Z. Several determinations are made on each component, as listed below. For each of the four components, values of σ (for a single determination) are 0.08% W, 0.20% X, 1.0% Y, 0.6% Z. Calculate σ for the sum of the means. Is there a significant difference between the sum of the means and 100%?

% W: 1.17, 1.08, 1.19, 1.20

% Y: 45.8, 46.4, 45.3, 46.3

% X: 49.8, 49.5, 49.8, 49.7

% Z: 1.5, 2.7, 1.7, 2.1

Ans. σ of the sum is 1.2%; no.

Section 5H

S1. A buret reading may be made with a σ of 0.010 ml. What are the absolute and relative σ 's in a measured volume of 20 ml? Compare answers with those of Prob. 6, Sec. 5H (p. 62).

Ans. 0.014 ml, 0.07%.

S2. Z is a sum of ten quantities, each with a standard deviation of σ .

(a) Estimate the "maximum error" of the sum, Z , by the reasoning of Sec. 5H.4 (p. 57). (Assume that the maximum error in each component quantity is 2σ . Why?)

(b) What is the probability that the maximum error of the sum will be exceeded? Does this maximum error have much meaning?

S3. Calculate the σ of the sum of two quantities, X and Y , with standard deviations x and y . In attempting to reduce the σ of the sum by reducing y , explain why it is not worth while to reduce y much below one-half x .

S4. Perform the following computations, using only a slide rule:

(a) 29.524×1.0103

(f) $1.0033/1.0020$

(b) 29.524×0.99730

(g) $(1.0043)^2$

(c) 29.524×1.0293

(h) $(1.0043)^4$

(d) $29.524/0.99730$

(i) $\sqrt{1.0043}$

(e) $95.927/96.325$

(j) $(1.0043)^{3/2}$

S5. Using the approximations of page 643, or methods like those used in deriving them, show that:

(a) $\sqrt{ab} = (a + b)/2$, if a is nearly equal to b .

(b) $(1 \pm x)^n(1 \pm y)^m = 1 \pm nx \pm my$, if $x, y \ll 1$.

S6. In a certain potentiometric method of analysis for chloride, the chloride concentration, C , is computed as $\log C = A - B$. Obtain an expression for the standard deviation of C in terms of the standard deviations of A and B .

S7. The value of a solubility product is sometimes computed from an equation of the type, $K = (A + B)D^2$. Calculate the standard deviation, k , of the solubility product, K , due to the standard deviations a , b , and c of A , B , and D , respectively.

Ans. $k^2 = (a^2 + b^2)D^4 + 4K(A + B)d^2$.

S8. Repeat Prob. S7 if the expression for K is $(A + B)^2D$.

THE ANALYTICAL BALANCE

THEORY AND CONSTRUCTION OF THE ANALYTICAL BALANCE

Distinction between Mass and Weight

(See Sec. 7A.1, p. 70)

The analyst is interested not so much in the weight as in the mass of an object. The mass, which is the amount of matter in an object, is a fixed, fundamental property of the object, independent of its surroundings. The *weight* of this object is the effect (force) of the gravitational field on the mass of this object, and is directly proportional to the mass. The relation is given by Newton's second law of motion,

$$f = mg$$

where f = weight of object, due to the force of gravity

m = mass of object

g = acceleration due to gravity

The weight, therefore, is not a property of the object alone, but is dependent upon the strength of the gravitational field in which the object is placed. The strength of the gravitational field of the earth changes appreciably with locality, so that the weight of an object is not constant, and is not as fundamental a property of the object as is the mass.

The usefulness of the balance arises in that it allows evaluation of the mass of an object by comparison with an equal amount of known, standard mass. In the balanced position, the force due to gravity on the object mass is equal to that on the known mass:

$$f_{\text{obj}} = f_{\text{std mass}}$$

$$m_{\text{obj}} \times g = m_{\text{std mass}} \times g$$

$$m_{\text{obj}} = m_{\text{std mass}}$$

Therefore, the mass of the object is equal to that of the standard mass, no matter what the value of g . This would not be true of weighings made on a spring balance at different geographical locations.

The standard masses used for comparison are erroneously called "weights," but this usage is so common that it is futile to attempt correction. The set of "weights" used in weighing really should be called a set of "masses." In most applications, however, the distinction is unnecessary. In quantitative analysis, the distinction may be ignored (except for the theory of the balance), and common usage is followed by using the term "weight" rather than "mass" in the remainder of this book.

The standard of mass is the gram, which is one-thousandth of the mass of a standard platinum-iridium bar that is kept at the International Bureau of Weights and Measures, near Paris, France. The mass of this bar was originally selected to be identical with that of 1000 cc of water at the temperature of its maximum density, 3.98°C. However, the original maximum density on which this selection was based has since been more accurately measured. The mass of 1000 cc of water is believed at present to be 999.972 g. It is not considered feasible to readjust the standard gram or the cubic centimeter to bring them into precise agreement. The agreement is still good enough so that for all except the most exact measurements the volume of one kilogram of water is 1000.0 cc at the temperature of maximum density.

Sensitivity of the Balance

(See Sec. 7A.2, p. 71)

Theory of balance sensitivity. Figure S7.1 represents schematically two positions of a balance such as that shown in Fig. 7.1 (p. 71). This balance has a center of gravity of mass M for the beam-pointer system, lying at a distance r below the fulcrum.* The pointer length is R , and L is the length of each balance arm. In the balanced condition, with equal masses m in each pan, the center of gravity (c.g.) lies vertically below the fulcrum, and the pointer falls at the scale center.

When an increment of mass, Δm , is added to the right-hand pan, the beam tilts out of the horizontal by an angle θ , and assumes a new equilibrium position. The c.g. moves a distance x out of the vertical plane through the fulcrum, and the pointer moves a distance X over the scale.

*The loads applied to the two pan knife-edges are not included in this center of gravity, since it is assumed that all three knife-edges lie in the same plane. In this case, since the pan loads are always very nearly equal, the center of gravity of the pan-load system falls at the fulcrum and can therefore exert no moment about the fulcrum. The pan load, then, does not affect the sensitivity.

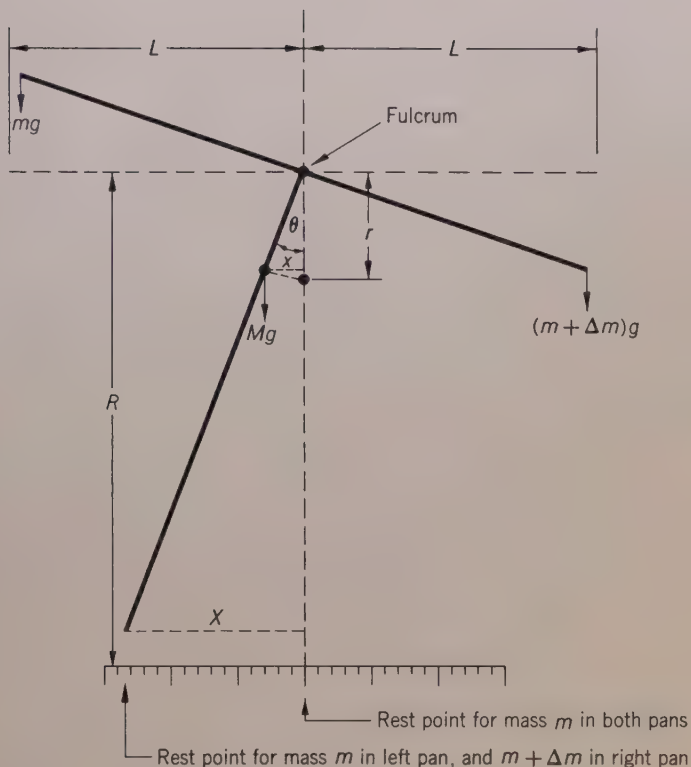


FIG. S7.1. Sensitivity of the Balance

In this new equilibrium position, the clockwise moments about the fulcrum must equal the counterclockwise moments.

$$(m + \Delta m)gL \cos \theta = mgL \cos \theta + Mgx \quad (Sa)$$

$$\Delta m = \frac{Mx}{L \cos \theta} \quad (Sb)$$

From the geometry of similar triangles,

$$\frac{x}{X} = \frac{r}{R} \quad (Sc)$$

Eliminating x between Eqs. *Sb* and *Sc*, and with θ being small,

$$\Delta m = \frac{rXM}{LR} \quad (Sd)$$

Rearranging Eq. *Sd*, and using the definition of sensitivity from Eq. 7.2 (p. 72),

$$\text{Sensitivity} = \frac{X}{\Delta m} = \frac{LR}{Mr} \quad (Se)$$

Equation *Sd* shows that the pointer displacement along the scale is proportional to the mass increment. Equation *Se* shows quantitatively the relationship between sensitivity and balance characteristics, as summarized on page 72.

Dependence of sensitivity upon load. In the preceding section, it was assumed that the three knife-edges lie in the same plane, as shown in Fig. S7.2*a*. For such a balance, the sensitivity is independent of the load; the pan-load c.g. is at the fulcrum and can exert no moment about the fulcrum.

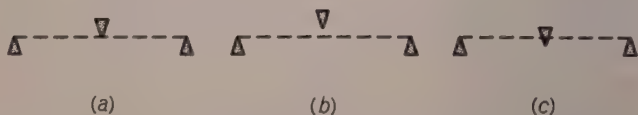


FIG. S7.2. Configuration of Pan and Beam Knife-Edges (Reprinted from I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 3d ed. [New York: Macmillan, 1952], Fig. 49, by permission of the publisher.)

Actually, however, the three knife-edges cannot be aligned perfectly enough to make the sensitivity independent of load. If the c.g. of the pan-load system is located below the fulcrum (Fig. S7.2*b*), this c.g. exerts a net restoring moment when the beam is tilted. The mass of the pan-load c.g. increases with loading, and the sensitivity of this type of balance therefore decreases as the load increases (Fig. 7.2*b*, p. 72). The greater the distance between the fulcrum and the pan-load c.g., the more the sensitivity varies with load. If the knife-edges are arranged as in Fig. S7.2*c*, similar considerations show that the sensitivity increases with an increase in load, as shown in the low-load part of Fig. 7.2*a*.

As the knife-edges of a balance become worn, the pan-load c.g. drops farther below the fulcrum; the sensitivity of a worn balance therefore varies more with load than does the sensitivity of a new balance. Figure 7.2*c* is a sensitivity curve that is typical for a worn balance.

A theoretical treatment shows that the sensitivity depends in an inverse manner upon the load, provided that there is no flexure of the beam (M24). Flexure in a well-constructed balance is negligible for loads not exceeding the capacity of the balance. If the load exceeds the capacity by several times, flexure may set in and the sensitivity may begin to decrease rapidly with load.

Period of the Balance

(See Sec. 7A.3, p. 73)

The period or time of oscillation of the balance depends upon many of the same factors as the sensitivity. A short period is desirable for rapid weighing; 10–20 seconds (5–10 seconds per swing) is acceptable for the ordinary balance.

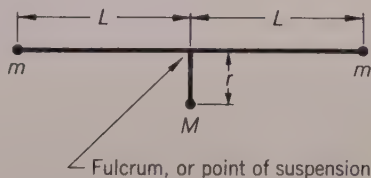


FIG. S7.3. The Balance as a Compound Pendulum

The balance of Fig. S7.1 is nothing but a compound pendulum, which is redrawn in Fig. S7.3, reduced to simplest terms. The symbols have the same meaning as in Fig. S7.1. The period of such a pendulum is given in any elementary physics textbook as

$$T = 2\pi\sqrt{I/Mgr} \quad (Sa)$$

I is the moment of inertia of the system, and may be calculated as

$$I = Mr^2 + 2mL^2 \quad (Sb)$$

Eliminating I between Eqs. Sa and Sb ,

$$T = 2\pi\sqrt{\frac{1}{g}\left(r + \frac{2mL^2}{Mr}\right)} \quad (Sc)$$

For all loads except the very smallest, $r \ll 2mL^2/Mr$, and

$$T = 2\pi L\sqrt{2m/Mgr} \quad (Sd)$$

From Eq. Sd , it may be seen that any attempt to increase sensitivity by increasing L , or by decreasing M or r , is accompanied by a disadvantageous increase in the period. In the construction of the analytical balance, a compromise must be achieved between high sensitivity and short period, for these two characteristics are mutually exclusive.

CONSTRUCTION AND TOLERANCES OF ANALYTICAL WEIGHTS

(See Sec. 7B, p. 75)

The National Bureau of Standards specifies five classes of weights that are suitable for quantitative analysis. *Class M* weights are of primary standard quality; they are used only to calibrate other weights, and are

not used in ordinary weighing operations. They are of one-piece construction, carefully machined to very close tolerances, and are plated with gold, platinum, or rhodium for protection against corrosion.

Class S weights are also highly accurate, and are used for calibration and for highly accurate analytical work. The integrals are made from brass or stainless steel; although they may be plated, they are usually lacquered for protection. Class S integral weights are of two-piece construction, the knob being threaded into the body to cover a small cavity. Small pieces of wire or foil (tantalum, aluminum, copper, or tin) are placed in the cavity by the manufacturer to adjust the mass of each weight within the specified tolerance. Class S fractionals are generally made from platinum, gold, or tantalum, but aluminum may be used for weights of 30 mg or less.

Class S-1 weights are similar in design and construction to Class S weights, but tolerance limits are several times greater. They are used for ordinary analytical work. Class P weights (formerly S-2) are suitable for routine analysis where only moderate accuracy is required. They are similar in construction to Class S weights, except that all frac-

TABLE S7.1
TOLERANCE LIMITS FOR DIFFERENT CLASSES OF ANALYTICAL WEIGHTS*

DENOMINATION	TOLERANCES (mg)†						
	CLASS M		CLASS S		CLASS S-1		CLASS P, OR S-2
	Individual	Group‡	Individual	Group‡	Individual	Group	
100 g.....	0.5		0.25		1.0		2.0
50.....	.25		.12		0.6		1.2
30.....	.15		.074		0.45		0.90
20.....	.10		.074		0.35		0.70
10.....	0.05		0.074	} 0.154	0.25		0.50
5.....	0.034		0.054		0.18		0.36
3.....	.034		.054		0.15		.30
2.....	.034	} 0.065	.054	} 0.105	0.13	Two-thirds of the weights in a set must be within one-half of the individual tolerances.	.26
1.....	0.034		0.054		0.10		0.20
500 mg.....	0.0054		0.025		0.080		0.16
300.....	.0054		.025		0.070		.14
200.....	.0054	} 0.0105	.025	} 0.055	0.060		.12
100.....	0.0054		0.025		0.050		0.10
50.....	0.0054		0.014		0.042		0.085
30.....	.0054		.014		0.038		.075
20.....	.0054	} 0.0105	.014	} 0.034	0.035		.070
10.....	0.0054		0.014		0.030		0.060
5.....	0.0054		0.014		0.028		0.055
3.....	.0054		.014		0.026		.052
2.....	.0054	} 0.0105	.014	} 0.034	0.025		.050
1.....	0.0054		0.014		0.025		0.050

* Data taken in part from Lashof and Macurdy, "Precision Laboratory Standards of Mass and Laboratory Weights," National Bureau of Standards Circular 547, Sec. I, August, 1954, Tables 6, 7, and 8, with permission of the publisher.

† Acceptance tolerances are given. Maintenance tolerances of twice the acceptance tolerances are allowed (after a set has been used) for Class M weights from 500 to 100 mg, inclusive, and for Class S weights above 100 mg.

‡ Any combination of the bracketed weights must fall within the group tolerances.

tionals may be of aluminum. *Class J* weights are especially for micro-analysis; they range from 50 to 0.05 mg, with individual tolerances of only 0.003 mg for each weight.

Class tolerances of analytical weights are given in Table S7.1 (U3).

Riders are usually made of aluminum. Most balances are designed in either of two ways for riders of different weights. If the zero on the rider scale is over the fulcrum, the rider weight in milligrams is indicated by the graduation mark on the rider scale directly over the right pan knife-edge. If the zero on the rider scale is over the left pan knife-edge, the rider weight is given by the graduation mark on the rider scale directly over the fulcrum. Common rider sizes are 5 and 10 mg, although odd sizes exist for special or older balances. It should always be verified that the rider is of the proper weight for the balance at hand.

WEIGHING PROCEDURES

Theory of Balance Oscillations

(See Sec. 7C.1, p. 76)

Balance swings are *damped* by friction and air resistance. Each swing is smaller than the preceding one by a constant quantity, called the *decrement*. In Fig. S7.4, S_1, S_2, S_3, \dots are a series of consecutive damped swings, each S representing the scale reading at the end of a pointer swing.* The amplitude (distance from the r.p. to the end of the swing) of each swing decreases by the decrement d from the amplitude of the previous swing.

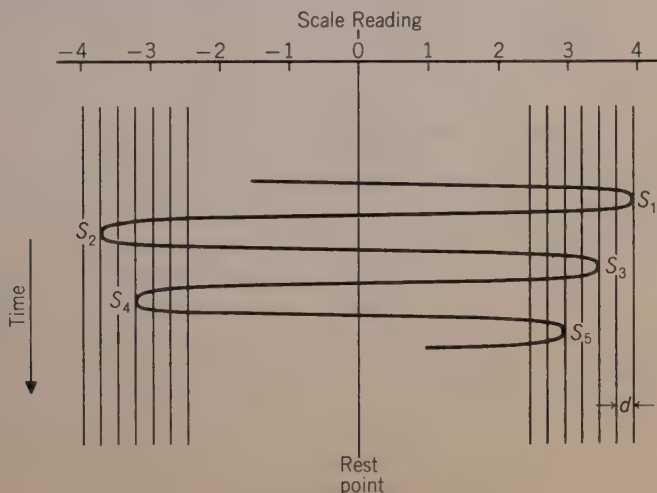


FIG. S7.4. Damped Balance Oscillations

*Note that for the figure shown, S_1, S_3, \dots are positive, whereas S_2, S_4, \dots are negative. The equations developed, however, are perfectly general.

If there were no damping, the r.p. could be estimated simply as the average of the two successive readings. For the damped balance, the amplitude of the second swing is less than the first by the decrement d , and the r.p. may be seen from Fig. S7.4 to be

$$\text{r.p.} = \frac{(S_1 - d) + S_2}{2} \quad (Sa)$$

In making a weighing, d may be estimated from the difference between any two successive swings to the same side. Thus

$$S_1 - S_3 = 2d \quad (Sb)$$

Elimination of d between Eqs. Sa and Sb gives

$$\text{r.p.} = \frac{S_1 + S_2 - (S_1 - S_3)/2}{2} \quad (Sc)$$

Rearranging Eq. Sc , we have

$$\text{r.p.} = \frac{(S_1 + S_3)/2 + S_2}{2} \quad (Sd)$$

For obtaining the r.p. from three consecutive pointer readings, Eq. Sd is a mathematical description of the averaging process given for the method of long swings (p. 77). The same reasoning may be applied to any odd number of consecutive swings. More rigorous methods of finding the rest point have been described ($S26$).

Single-Swing Method of Weighing

One side of the balance, usually the left, is made definitely heavier than the other by adjusting the nuts, G (Fig. 7.3, p. 74), so that the pointer swings to about six divisions right of center when the unloaded balance is freed. The extremity of this first swing is called the *index*. For the empty balance it is called the *zero index*, and for the loaded balance, the *load index*. Because of damping and inertia, the change of the index is not proportional to the weight difference between pans, as is the case with rest points. In weighing an object, therefore, the rider is adjusted until the load index becomes equal to the zero index, at which point the weight of the object may be taken as identical with the weights. In adjusting the rider it is helpful to know approximately the sensitivity of the balance (that is, the change in index per milligram).

It should be easy to see that the magnitude of the first swing is de-

pendent upon the period and inertia of the balance. Since these vary with load, error is theoretically inherent in the single-swing method. In most analyses, however, sample weights are obtained as differences between two weighings. Since these differences are almost always small (1–2 g), the change in index is small, and the error in the single-swing method is negligible. For a heavy sample, the error may be appreciable and may amount to a milligram on balances that show a considerable change of sensitivity with load. Even in such cases, since the sample is heavy, the percentage error is still small and is usually negligible (B26).

With the single-swing method, the pan arrests must be carefully adjusted, so that they give no impulse to the pans when lowered. It is also necessary to center the pans by pushing the arrests up and down a few times before releasing the beam; otherwise the pans swing independently about their knife-edges and cause irregularity in the index.

In practiced hands the single-swing method is very fast, and sufficiently accurate for ordinary analytical work. A student should use this method only if all other people who use the balance are willing to use the same method. More time is lost than saved if the balance must be readjusted frequently.

DETERMINE ERRORS IN WEIGHING

Double Weighing. Rigorous Derivation of Eq. 7.4

(See Sec. 7D.2a, p. 81)

The elementary mode of deriving Eq. 7.4 (p. 83) contains hidden assumptions that are brought out in the following derivation. All symbols have the meanings defined previously.

$$\text{For the object on the left pan,} \quad mL_l = m_r L_r \quad (Sa)$$

$$\text{For the object on the right pan,} \quad m_l L_l = mL_r \quad (Sb)$$

Eliminating L_l and L_r from Eqs. *Sa* and *Sb*, and solving for m , we have

$$m = \sqrt{m_r m_l} \quad (Sc)$$

Equation *Sc* is the exact way to calculate m , and Eq. 7.4 is merely a good approximation, since m_r and m_l are nearly equal (Prob. S5, Sec. 5H, p. 648).

Calibration of Weights

(See Sec. 7D.2b, p. 83)

The simplest and most direct calibration procedure is to weigh each weight in the set to be calibrated against its counterpart in a known,

standard set, either by substitution or by double-weighing. After each weight has been calibrated, it is highly desirable to check a few combinations of weights against each other in order to reveal errors, if any. In this way, calibration corrections may be obtained for each member of the set in question. The *calibration correction* is defined as the number of milligrams that must be added to the denomination of the weight to give the correct value. Thus, if a 10-g weight is found to weigh only 9.99991 g, the calibration correction is -0.09 mg. A typical set of calibration corrections is shown in Table S7.2. In using calibration corrections it is best to sum the denominations of all the weights used for the weighing, and then to apply the sum of the calibration corrections as a single correction on the sum of the denominations. This is preferable to summing the correct values of the individual weights.

TABLE S7.2

CALIBRATION CORRECTIONS ON A TYPICAL SET OF CLASS S WEIGHTS

Denomination (g)	Correction (mg)	Denomination (g)	Correction (mg)
50.....	0.18	0.500.....	-0.02
20.....	0.00	0.200.....	0.02
10.....	0.05	0.100.....	0.01
10'.....	-0.02	0.100'.....	0.01
5.....	0.03	0.050.....	-0.02
2.....	0.05	0.020.....	-0.01
2'.....	0.05	0.010.....	-0.01
1.....	0.00	0.010'.....	-0.01
		0.010 (rider).....	0.00 (adjusted)

It is not a severe disadvantage of the direct calibration procedure that a whole set of standard weights is required, for a worker almost always has temporary access to a reliable set of weights with which to calibrate his set. There are more precise calibration procedures, like that of T. W. Richards, that require the use of only one standard weight. These procedures are necessary only in analyses of extremely high accuracy, and are spurious for ordinary analytical work at the 0.1% error level. Benedetti-Pichler outlines and discusses such a calibration procedure (B9).

Error Due to Air Buoyancy

(See Sec. 7D.2c, p. 83)

Figure S7.5 illustrates three different cases of the buoyant effect of air. Assume that an object in the left pan is exactly counterbalanced in air by weights in the right pan, and that the air is then removed. If the object has a lower density than the weights, the volume of the object is larger (Fig. S7.5a), and the buoyant effect on the object is greater. Removal of the air then causes the left pan to sink, and more weight has

to be added to the weight pan to reach a counterbalance. Thus the mass of the object in vacuum is greater than that measured in air, a conclusion in accord with Eq. 7.5 (p. 83). In Fig. S7.5*b* the object and weights have the same density and therefore the same volumes. Removal of air removes the same buoyant effect from both pans, and the counterbalance is maintained in vacuum. In this case the mass of the

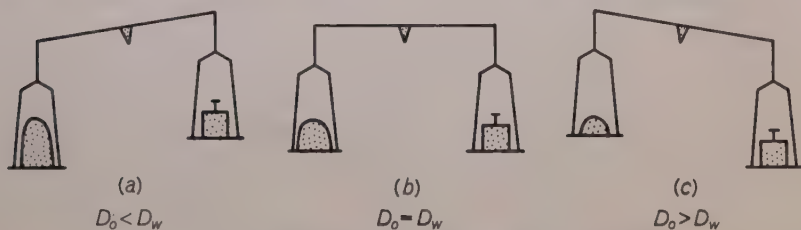


FIG. S7.5. Removal of Buoyant Effect in Weighing

object in vacuum is the same as that measured in air. In Fig. S7.5*c* the object is more dense than the weights, and the mass of the object in vacuum is less than that measured in air.

The buoyant effect on an object is equivalent to the mass of air displaced, and it may be calculated as

$$\text{Buoyancy} = \left(\frac{\text{ml of air}}{\text{displaced}} \right) \times \left(\frac{\text{density of}}{\text{air, g/ml}} \right) \quad (\text{Sa})$$

$$\text{Buoyancy} = \frac{\text{mass of object, g}}{\text{density of object, g/ml}} \times 0.0012 \text{ g/ml} \quad (\text{Sb})$$

It is sufficiently accurate in ordinary analysis to take the density of air as 0.0012 g/ml.

If the buoyancies on the object and weights are calculated according to Eq. Sb, the buoyancy correction (Eq. 7.5) becomes

$$\frac{m_o}{D_o} (0.0012) - \frac{m_w}{D_w} (0.0012) \text{ g} \quad (\text{Sc})$$

D_o and D_w are the densities of the object and weights, respectively. Because the buoyancy correction is small and need not be precisely known, m_o may be approximated as m_w . The buoyancy correction then becomes

$$0.0012 m_w \left(\frac{1}{D_o} - \frac{1}{D_w} \right) \text{ g} \quad (\text{Sd})$$

Densities of materials used for weights are, in grams per milliliter, Al, 2.7; stainless steel, 7.8; brass, 8.0; Ta, 16.6; Au, 19.3; Pt, 21.4.

Example. If a sample of water (density = 1.00 g/ml) weighs 1.0000 g in air, using brass weights, what is the weight in vacuum?

$$m_o = 1.0000 + (0.0012)(1.0000) \left(\frac{1}{1.00} - \frac{1}{8.0} \right) = 1.0011 \text{ g}$$

The buoyancy correction is only 1.1 mg, or 0.11% of the sample weight.

Since the weight of a sample is always obtained as a difference in weights of a container before and after adding the sample, it is not necessary to apply buoyancy corrections to the container or to those particular weights that are used in both weighings. Only the sample itself and those weights that are not used in both weighings need be corrected for buoyancy; this is important when weights consisting of different materials are used, such as integrals of brass and fractionals of Al.

For most solid samples or precipitates, the buoyancy correction is negligible in ordinary analysis. A typical nonmetallic solid sample weighs about 1 g and has a density of 3 g/ml. When weighed in air against brass weights, the buoyancy correction is about 0.3 mg, from Eq. *Sd*. This is only 0.03% of the sample weight.

Not only is the buoyancy correction small, but in all analyses where the purpose is to find the percentage of a constituent, a ratio of weights is taken, and the buoyancy corrections tend to cancel. This same reasoning applies to most volumetric analyses if buoyancy corrections are omitted in both standardization and in analysis.

Theoretically, variations in barometric pressure and accompanying variations in air density cause variations in the weight in air of a given object. The fluctuation of pressure between weighings of a container is seldom greater than 30 mm of mercury in 750, or about 5%. This causes a 5% variation in buoyancy, which is negligible for ordinary quantitative analysis. Again, this is not true when a small difference in the weight of an object of large volume is measured, which is often the case in microchemical analysis. Here buoyancy corrections must be made very carefully and precisely, and errors due to moderate fluctuations in atmospheric pressure may be appreciable. The use of a *counterpoise* of identical volume provides perfect elimination of error due to variations in atmospheric pressure, and this is a standard technique in microchemical analysis.

OTHER TYPES OF BALANCES

(See Sec. 7E, p. 84)

The weighing process has undergone tremendous improvement within the past two decades. Generally, the improvement has followed two lines—increased sensitivity and increased speed and ease in weighing.

The following types of balances and accessories are among those that the student is most likely to encounter in quantitative work beyond the elementary course.

In Table S7.3 the sensitivities and capacities of various kinds of balances are contrasted. This table should be compared with Table 2.1 (p. 8).

TABLE S7.3
COMPARISON OF VARIOUS TYPES OF BALANCES

Type	Capacity (g)	Standard Deviation (mg)
Oversize	2000	5
Ordinary	200	0.1
Semi-micro	100	0.01
Micro	20	0.001
Ultramicro	0.025	0.00002

The Single-Pan Balance

One of the newest developments in weighing is the single-pan balance, shown in Figs. S7.6 and S7.7. A load in the pan is balanced by removing an equivalent amount of rider-type weights that hang upon the same arm of the balance as the pan. Weighing is therefore done by the method of substitution. The weights are removed with controls that operate from the outside of the case, the weight being read from an illuminated scale in the front panel. Air damping is employed. Only a fraction of a minute is required per weighing. Various models range in sensitivity from 10 mg/div to 0.005 mg/div. Since the weights are built in and never handled by the user, calibration and maintenance problems are virtually nonexistent.

The Microbalance

Surprisingly, when greater sensitivity is desired than that obtainable with the ordinary balance, it is necessary to reduce rather than increase the balance dimensions. When the lengths of the beam and the pointer are decreased, the loss in sensitivity is more than offset by other gains, such as decreased mass at the center of gravity and greater precision in construction. Microbalances vary greatly in design, but most of them have rather short beams (3–5 inches) and lower capacities (1–20 g) than the ordinary balance.

The sensitivity of a typical microbalance is 10 γ /div. The rider is around 5 mg, moving in 0.1-mg notches on the beam. Magnifying glasses or projection reading devices are generally used to read the rider position and pointer scale, since the divisions are so small.



FIG. S7.6. A Single-Pan Balance (Reproduced by courtesy of E. H. Sargent & Co.)

The construction of microbalances requires care far exceeding that used for ordinary balances. For a microbalance with a 20-g capacity and a standard deviation of 1 γ , a positional accuracy of 1 in 20 million is required. Knife-edges must be positioned to 1-millionth of an inch on a 5-inch beam. Great care is also required in the choice of materials and machining methods, so that the positions remain permanent in use.

The techniques required for weighing on the microbalance are considerably more complicated than those for ordinary weighing (C7, H13). Indeterminate errors due to electrification, humidity, temperature

gradients, and atmospheric changes must be guarded against very exactly. Much study has been made of the reduction of determinate errors due to inequality in lengths of balance arms, weights, and buoyancy.

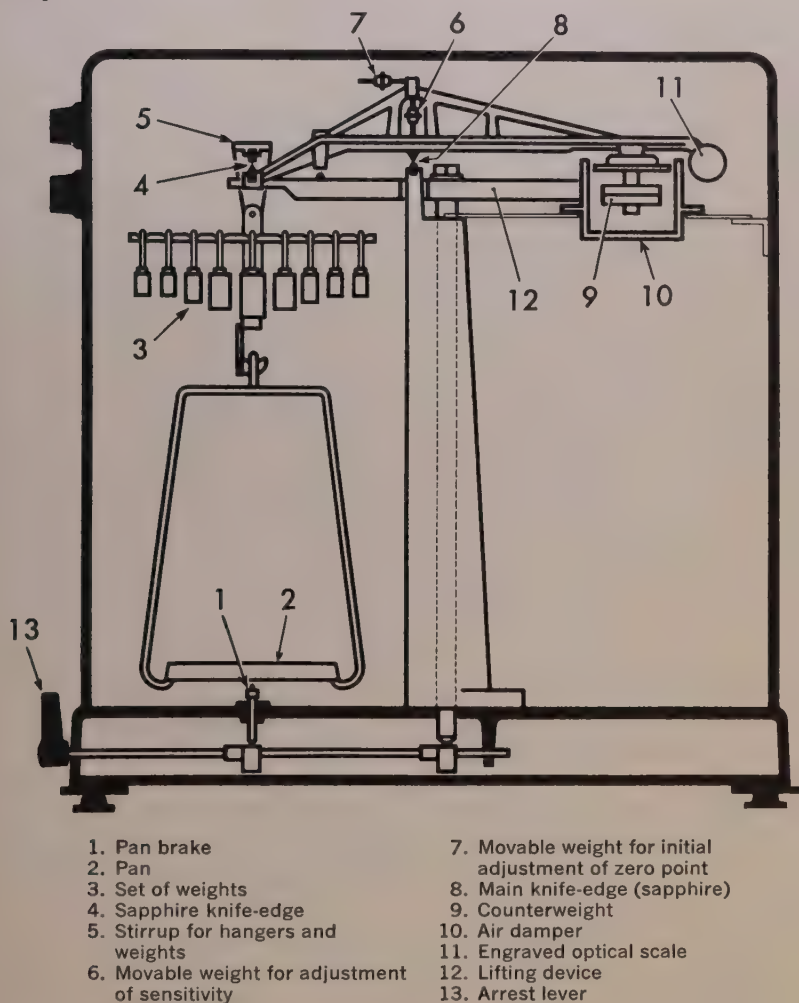


FIG. S7.7. Schematic of a Single-Pan Balance (Reproduced by courtesy of E. H. Sargent & Co.)

Intermediate between the ordinary and microbalances are the semi-microbalances. They have capacities of about 100 g and a standard deviation of about 0.01 mg.

Ultramicrobalances

Most ultramicrobalances are of three types: (1) pivotal, with a fulcrum at the center of a quartz-fiber beam (C13), (2) helical, essentially a spring balance made from a coiled quartz fiber, (3) torsional, like that shown schematically in Fig. S7.8.

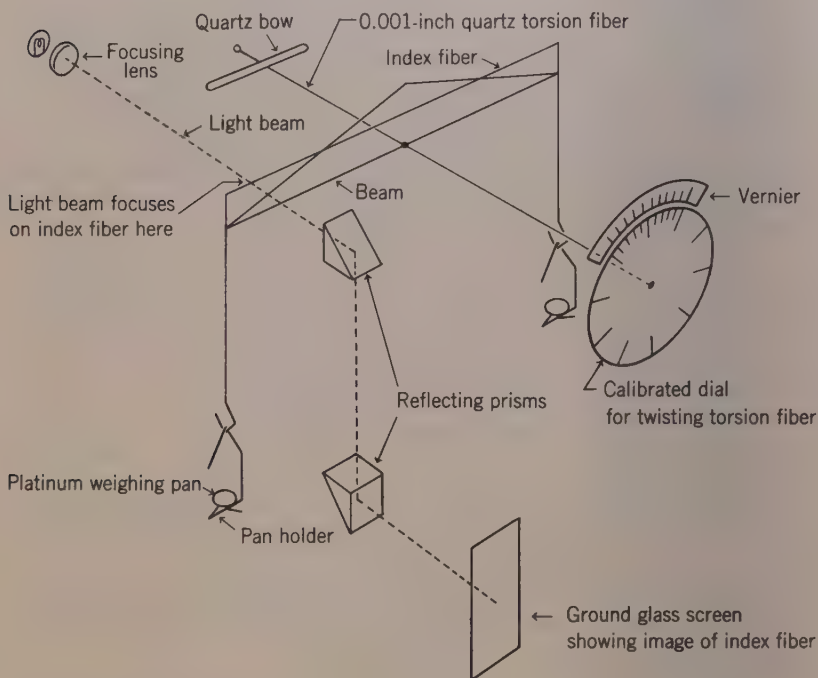


FIG. S7.8. Quartz-Fiber Torsion Ultramicrobalance (Redrawn from G. T. Seaborg and B. B. Cunningham, *Chemical and Engineering News*, 24, 1192 [1946]. Copyright 1946 by the American Chemical Society and redrawn by permission of the copyright owner.)

The quartz-fiber torsion microbalance has a capacity of 25 mg and a standard deviation of 0.02γ (2×10^{-8} g). The beam is a quartz-fiber network, about four inches long, attached at its center to a taut horizontal quartz torsion fiber at right angles to the beam. Pans hang from quartz fibers at the ends of the beam. The heaviest of the fibers is only a few times the thickness of a human hair. Inequality in loading causes a deflection of the beam and a twisting of the torsion fiber. The unbalance is measured by the amount of twisting in the opposite direction required to restore the beam to the horizontal position. Movement of

the beam is observed through an optical magnifying system. The whole assembly is housed in an insulated chamber.

Electromagnetic Balance

The electromagnetic principle may be applied to weighing by coupling the balance pointer to the coil of a d'Arsonval galvanometer movement. A load in the pan causes a displacement of the coil, which is brought back to null by a measured current that is proportional to the load. The range of the Cahn microbalance is adjustable to 5 mg or 50 mg full scale. Calibration is performed with a standard weight, so that the restoring current scale reads directly in mass units. A novel feature is that the pan compartment is removable, permitting weighings to be made in remote locations (M23).

Damping Devices

When fitted with a proper damping device, the balance does not oscillate about its r.p., but slowly approaches the r.p. in about the same time as is required for the undamped balance to complete a few oscillations. Good damping introduces a particular kind of resistance to the motion of the beam, this resistance being proportional to the velocity of motion and decreasing to zero as the equilibrium position is approached. A good damping device therefore does not decrease the sensitivity of the balance. With such damping, it is possible to read the r.p. directly, which eliminates the fatiguing process of watching the moving pointer.

Magnetic damping is most popular. A nonmagnetic vane or plate, usually of aluminum, is fixed to the beam, and passes between the poles of a stationary magnet. As the beam moves, the plate moves in the magnetic field, and eddy currents are set up that oppose the motion. Some balances are equipped with built-in but movable magnetic dampers, which may or may not be used, according to preference. There are magnetic damping units that may be attached to any type of balance.

In some balances air damping is convenient. A piston is attached to the beam and moves freely but closely inside a concentric, stationary cylinder. Resistance of the air between the piston and cylinder damps the oscillation of the balance. These devices are less widely used than magnetic ones because of their massiveness. The single-pan balance is air damped.

MAINTENANCE AND REPAIR OF BALANCE AND WEIGHTS

(See Sec. 7F, p. 85)

Most balance adjustments may be made by any mechanically inclined laboratory worker. The labor is lightened if a kit of a few special tools

is kept by the instructor in charge of the course. For some repairs the services of a machinist or even a balance expert may be necessary, but not many such occasions arise during a semester. Elementary servicing of the ordinary balance is excellently described in the short, practical monograph by MacNevin (M3).

The symptoms uncovered in Exp. 7.1 usually suggest their own remedies. Generally, if any item is clean and works properly, it should be left alone. All cleaning should be done with a lintless cloth or chamois that has been washed and dried. A damp cloth or chamois may be used for the windows and floor. No liquid solvents of any sort should be used inside the balance case, since they may remove protective finishes. Lubricants catch dust, and none should be used inside the balance case. If swings are smooth, knife-edges and bearing plates should be left alone. If necessary, they may be cleaned by light rubbing with a chamois-wrapped splint.

Only a small proportion of the weights will go out of tolerance during a semester, and, of these, the majority can be easily repaired. After a few dozen defective weights of the same denomination are accumulated, reclamation is worth while. The weights should be carefully wiped clean with a cloth, brushed free of lint, and polished with chamois. Bent fractionals may be straightened with chamois-tipped pliers. Badly damaged weights are scrapped or sent to the manufacturer for refinishing.

All weights up through 2 g should be adjusted within 0.1 mg of their denominations. Higher integrals are adjusted within 0.5 mg. Two-piece integrals may be adjusted as follows: The weight and unscrewed knob are weighed in one balance pan against a standard weight in the other pan. Small pieces of 1–5 mil Ta wire are added to the cavity until the proper weight is obtained. (Standard wire pieces may be obtained ready-cut from balance manufacturers.) The knob is then screwed back.

Fractionals and one-piece integrals may be reduced in weight by being filed finely along one edge. Weights may be built up with a lacquer solution prepared from 2.5 g of orange shellac dissolved in 250 ml of 95% ethyl alcohol and filtered through a coarse filter paper. Slightly more solution than is needed is dropped onto the weight with a micro-pipet, and then the lacquer is allowed to dry for a few minutes at room temperature and baked for a half hour at 50°C. The fractional weight is finally reduced by filing, if necessary.

SUPPLEMENTARY QUESTIONS

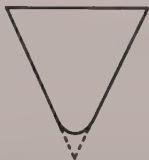
Sections 7A–C

S1. Explain how the analytical balance measures mass, whereas the spring balance measures weight.

S2. Discuss the effect on sensitivity of the following changes, assuming that all other factors remain unchanged.

(a) Permanent deformation of the beam, so that the pan knife-edges are lowered below the center knife-edge.

(b) Wearing of the center knife-edge as shown in the accompanying figure.



S3. The beams on older balances were sometimes made from brass, coated with lacquer to prevent corrosion. The 0-r.p. of such balances usually changed with relative humidity. Explain.

S4. Explain why the higher Class M weights have larger tolerances than the corresponding Class S weights.

S5. Speculate on the details of how one-piece Class M standard weights may be adjusted within the narrow tolerances of Table S7.1 (p. 654).

S6. Explain why neither a very long nor a very short swing is used for the zero index in the single-swing method.

S7. In damped swings the assumption that the decrement is constant is not valid over a large number of swings. Explain the consequences if it were.

Sections 7D, E

S1. Contrast the procedure for checking a weight set with the procedure for calibrations, and state when each is more appropriate than the other.

S2. Explain why moderate temperature changes cause no rider-weight errors in the 1-g notched-beam rider balance.

S3. Explain why the sensitivity of the single-pan balance is constant over a range of pan loads from 0 to 200 g. (Consider the sum of the weights plus object.)

S4. In using a sensitive microbalance at 25°C, it is found that the mere presence of the operator causes an irregular drifting of the 0-r.p. and contributes to the random error of weighing. This drift has been ascribed to the body temperature of the operator as he sits before the balance and manipulates the controls. Describe the means that you would use to reduce this random error.

SUPPLEMENTARY PROBLEMS

Sections 7A-C

S1. In an ordinary analytical balance, the distance between pan knife-edges is 15 cm. Modern balance manufacturers claim that the arms are equal within 1 part in 100,000. Within what distance of the exact midpoint between the pan knife-edges must the center knife-edge be located to satisfy this claim?

Ans. 4×10^{-6} cm.

S2. The acceleration due to gravity, g , is 977.99 cm/sec² at the equator, and 980.42 cm/sec² at Madison, Wisconsin. How much heavier in weight, percentage-wise, is the 10-g mass at Madison than at the equator? How many milligrams is this? Describe a scale or balance that would actually show the weight difference between the two localities.

S3. Assume that the balance of Fig. S7.1 (p. 651) has the following characteristics: $M = 20$ g; $r = 0.25$ mm; $L = 8.00$ cm; $R = 18.00$ cm. Calculate the sensitivity of this balance in millimeters per milligram. *Ans.* 2.9 mm/mg.

S4. For the balance of Prob. S3, at what load would the term r in Eq. Sc (p. 653) be only about 1% of the term $2mL^2/Mr$?

S5. Assume a balance to have the characteristics given in Fig. S7.1, and in addition, assume that the pan-load c.g. with a mass W lies at a distance d below the fulcrum. Find the dependence of sensitivity upon the balance characteristics.

$$\text{Ans. } \frac{X}{\Delta m} = \frac{LR}{Mr + Wd}.$$

S6. Assume that the balance of Prob. S5 has the following characteristics: $M = 20$ g; $r = 0.25$ mm; $L = 8.00$ cm; $R = 15.00$ cm; $d = 0.020$ mm. Calculate and plot the sensitivity in mm/mg for several values of W up to 400 g.

S7. Repeat Prob. S5 for the case in which the pan-load c.g. lies at a distance d above the fulcrum. If the balance characteristics are as in Prob. S6, at what value of W does the balance become unstable?

$$\text{Ans. } \frac{X}{\Delta m} = \frac{LR}{Mr - Wd}; 250 \text{ g.}$$

S8. Suppose that a balance is constructed for a 5-mg rider, but that a 12-mg rider is inadvertently used. What is the correct weight when the rider reads 8.3 mg?

S9. On a rider-type balance, the rider zero is over the left pan knife-edge, and the 10-mg mark is over the right pan knife-edge. What is the rider weight?

$$\text{Ans. } 5 \text{ mg.}$$

S10. Calculate relative tolerances for some of the weights in Table S7.1 (p. 654).

S11. In weighing an object in the left pan by the single-swing method, the load index is +5.6 with 32.6400 g in the right pan and the rider at 9.0 mg. The zero index is +7.0, and the sensitivity is unknown. A second adjustment of the rider to 8.0 mg changes the load index to +8.0. Approximately what should be the third position of the rider?

$$\text{Ans. } 8.4 \text{ mg.}$$

S12. It is only approximate to describe a damped oscillation as having a constant decrement. More accurately, the amplitudes of successive swings always stand in the same ratio to each other. Thus from Fig. S7.4 (p. 655), $S_1:S_2 = S_2:S_3 = S_3:S_4 = \dots$. Show that when these ratios are nearly unity (i.e., when the decrement, d , is small compared to the amplitude), d may be regarded as constant over a small number of swings (S26).

Section 7D

S1. Find the weight in vacuum of a sample of Al having a weight of 38.7619 g in air, using brass weights. *Ans.* 38.7733 g.

S2. Find the weight in vacuum of a piece of Au with a weight in air of 27.2413 g using brass weights.

S3. Find the weight in vacuum of a sample of Pb (density, 11.4 g/ml) from the following weights in air: weight of empty container, 27.0876 g; weight of container plus sample, 27.9134 g. Integral weights are brass, and fractionals are aluminum.

$$\text{Ans. } 0.8255 \text{ g.}$$

S4. It is desired to obtain 11.688 g of NaCl to prepare a liter of 0.2000 M solution. What weight must be weighed out in air, using brass weights?

S5. Find the weight in vacuum of a sample of water that weighs 34.9874 g in air against brass weights. Is it justifiable to express the answer to the nearest 0.1 mg?

$$\text{Ans. } 35.024; \text{ no.}$$

S6. An empty sample container with an air-tight stopper has a volume of 50 ml. At an atmospheric pressure of 755 mm of mercury, with the interior air pressure equalized to 755 mm, the closed container weighs 41.7691 g in air against brass weights. Calculate the weight of this container when the atmosphere drops to 742 mm pressure, assuming that the container has not been opened. Although this error could be serious if the container were used in weighing out a 0.1-g sample, state how the error could be rendered insignificant.

S7. A sample (density, 4.0 g/ml) weighs 1.0000 g in air and yields a precipitate of AgCl (density, 5.6 g/ml) that weighs 1.9763 g in air. Aluminum weights are used. If the % Cl is to be reported, calculate the relative error made by not correcting for buoyancy. Ans. 0.09 p.p.t.

S8. Set a limit to the sample density below which it is necessary to apply a buoyancy correction to keep the relative error due to buoyancy below 0.05%. Assume that brass weights are used. In a similar manner, set an upper limit.

S9. An object weighs 31.8763 g in air against brass weights, and has an *in vacuo* density of 3.000 g/ml. What would be the weight of this object immersed in water (density *in vacuo*, 1.000 g/ml)? Ans. 21.248 g.

S10. An object weighs 36.5431 g in air and 28.6396 g when immersed in water (density, 1.0000 g/ml). What is the density of the object?

S11. A glass bob (density, d_b g/ml) is suspended from one end of a balance beam by a thin platinum wire, so that it may be weighed while immersed in a liquid (density, d_l g/ml). Let the weights in air required to counterbalance the bob in air and liquid be m_w and m_l , respectively. Show that d_l is a linear function of $m_w - m_l$. This problem outlines the principle of the specific-gravity balance.

S12. With the 20-g weight in the right pan, and the 20'-g weight in the left pan, the r.p. falls 0.9 division to the left of the 0-r.p. The sensitivity is 3.0 div/mg. What conclusions may be drawn if the r.p. falls 1.7 divisions to the left of the 0-r.p. when the weights are interchanged?

COMPUTATIONS OF GRAVIMETRIC ANALYSIS

SELECTION OF SAMPLE SIZE TO SIMPLIFY COMPUTATIONS

(See Sec. 9B, p. 141)

If, in a particular type of analysis, the sample size S is chosen equal to the gravimetric factor F , Eq. 9.2 (p. 143) indicates that the percentage of sought-for constituent is numerically equal to one hundred times the weight of isolated precipitate. This virtually dispenses with computations. If an unworkable sample size is required when S is set equal to F , then a simple numerical relationship may be chosen, so that the percentage is a simple multiple or fraction of the weight, W . Computation is then reduced to multiplying W by a simple integer or fraction to obtain the result.

Such weights are called *selected sample weights*, or *factor weights of sample*. This technique is useful in routine work, where many analyses of the same kind are performed every day. The elimination of computations not only saves time, but also reduces the chances of error, and permits results to be computed by relatively unskilled help. The technique also may be applied to volumetric analysis. However, since the sample size must be adjusted in weighing, the method is not applicable to samples that change rapidly on exposure to air, or to samples that are not finely divided, such as alloy turnings. In making the weighings a fixed tare equal to the desired sample size is useful.

Example. What sample size should be selected so that each milligram of BaSO_4 obtained in a gravimetric analysis is equivalent to 0.002% S in a steel?

1 mole of S is equivalent to 1 mole of BaSO_4 .

1 mg BaSO_4 is equivalent to

$$\frac{1}{233.40} \times 32.064 = 0.137378 \text{ mg S}$$

mmoles BaSO_4 = mmoles S

Since 0.137378 mg S must represent 0.002% of the sample weight, x ,

$$0.00002x = 0.137378 \text{ mg}$$

$$x = 6868.9 \text{ mg} = 6.8689 \text{ g of sample}$$

The precision with which the sample should be weighed depends on the precision desired in the analysis.

INDIRECT ANALYSIS OF MIXTURES

(See Sec. 9D, p. 145)

Even if it is not possible to determine one component of a two-component mixture directly, and to obtain the other by difference, it may still be possible to determine both by indirect analysis. *Indirect analysis* depends on the fact that when two substances of different molecular weights are given identical chemical treatment, they experience relatively different changes in weight. Thus converting the mixture of the two substances in question to a different mixture, without separation, gives data in the form of simultaneous equations that may be solved for the amount of each substance in the original mixture. The following illustrative examples are gravimetric ones, but the indirect method is also applicable to volumetric determinations.

Example S1. A 1.0000-g sample contains only NaCl and KCl. These are converted to the sulfates by being fumed with conc. H_2SO_4 . The pure, dried sulfates weigh 1.1919 g. What are the percentages of NaCl and KCl in the original sample?

Let $X = \text{g NaCl}$ and $Y = \text{g KCl}$ in the original mixture.

Since

$$\text{g NaCl} + \text{g KCl} = 1.0000 \text{ g}$$

$$X + Y = 1.0000 \quad (a)$$

Also

$$\text{g Na}_2\text{SO}_4 + \text{g K}_2\text{SO}_4 = 1.1919 \text{ g}$$

$$\text{g Na}_2\text{SO}_4 = \underbrace{\frac{X}{58.44}}_{\text{moles NaCl}} \times \underbrace{\frac{1}{2}}_{\text{moles Na}_2\text{SO}_4} \times 142.04 \text{ g Na}_2\text{SO}_4$$

$$\text{g K}_2\text{SO}_4 = \underbrace{\frac{Y}{74.56}}_{\text{moles KCl}} \times \underbrace{\frac{1}{2}}_{\text{moles K}_2\text{SO}_4} \times 174.27 \text{ g K}_2\text{SO}_4$$

Therefore

$$\frac{142.04}{2 \times 58.44} X + \frac{174.27}{2 \times 74.56} Y = 1.1919 \quad (b)$$

Solving Eqs. a and b simultaneously for X and Y gives

$$X = 0.499 \text{ g NaCl} \quad \text{or} \quad \frac{0.499}{1.0000} \times 100 = 49.9\% \text{ NaCl}$$

$$Y = 0.501 \text{ g KCl} \quad \text{or} \quad \frac{0.501}{1.0000} \times 100 = 50.1\% \text{ KCl}$$

The answers for X and Y should be checked in Eq. a or b .

If the original sample contains other substances besides the sought-for pair, it is necessary to make two conversions to obtain the two required equations. In the conversions, the other substances must remain inert. The two conversions may be made either on two separate portions of the original sample, or consecutively on the same portion of the original sample. Example S2 illustrates the latter case.

Example S2. A 1.0000-g sample containing chloride and bromide among other non-interfering substances is treated with excess AgNO_3 , and 0.9560 g of mixed AgCl and AgBr is quantitatively recovered. Reduction of the silver halides gives 0.7065 g of metallic silver. What are the percentages of chloride and bromide in the original sample?

Let $X = \text{g Cl}$ and $Y = \text{g Br}$ in the original sample.
Since

$$\begin{aligned} \left(\frac{\text{g AgCl from}}{\text{original Cl}} \right) + \left(\frac{\text{g AgBr from}}{\text{original Br}} \right) &= \left(\frac{\text{g mixed}}{\text{Ag halides}} \right) \\ X \frac{143.32}{35.453} + Y \frac{187.78}{79.909} &= 0.9560 \end{aligned} \quad (a)$$

The second equation may be obtained by realizing that

$$\begin{aligned} \left(\frac{\text{g Ag from}}{\text{AgCl}} \right) + \left(\frac{\text{g Ag from}}{\text{AgBr}} \right) &= \left(\frac{\text{g Ag from reduction}}{\text{of halides}} \right) \\ \left(\frac{\text{g Ag from}}{\text{AgCl}} \right) &= X \frac{143.32}{35.453} \times \frac{1}{143.32} \times 107.870 \text{ g Ag} \\ &\quad \text{g AgCl} \quad \text{moles AgCl, or} \\ &\quad \text{moles Ag} \\ \left(\frac{\text{g Ag from}}{\text{AgBr}} \right) &= Y \frac{187.78}{79.909} \times \frac{1}{187.78} \times 107.870 \text{ g Ag} \\ &\quad \text{g AgBr} \quad \text{moles AgBr, or} \\ &\quad \text{moles Ag} \\ X \frac{107.870}{35.453} + Y \frac{107.870}{79.909} &= 0.7065 \end{aligned} \quad (b)$$

Solving Eqs. a and b for X and Y , we have

$$\begin{aligned} X &= 0.2184 \text{ g Cl} \quad \text{or} \quad \frac{0.2184}{1.0000} \times 100 = 21.84\% \text{ Cl} \\ Y &= 0.0311 \text{ g Br} \quad \text{or} \quad \frac{0.0311}{1.0000} \times 100 = 3.11\% \text{ Br} \end{aligned}$$

These answers should be checked in Eq. a or b .

To study the precision of indirect methods, suppose that the 1.0000-g sample of Ex. S1 contains pure NaCl. The weight of the sulfate obtained would be $1.0000 \times 142.04 / (2 \times 58.44) = 1.2153$ g. On the other hand, if the 1.0000-g sample contains pure KCl, the weight of sulfate obtained would be $1.0000 \times 174.27 / (2 \times 74.56) = 1.1687$ g. The whole range from 0 to 100% KCl is therefore represented by a weight range of the product sulfates from 1.2153 to 1.1687 g, or 0.0466 g. Thus each 0.1-mg error in this range represents an error of $100 \times 0.0001 / 0.0466 = 0.2\%$ KCl. In a mixture containing 50% KCl, this would be a relative error of $100 \times 0.2 / 50 = 0.4\%$. It may be seen that each 0.1-mg error in weight of the converted compounds (representing a relative error of only about 0.01%) is multiplied many times to a much larger relative error (0.4%) in the final result. A more rigorous analysis of the error may be made by the methods described elsewhere in the Supplement (pp. 640-43), giving the following general conclusions as to the accuracy of indirect methods.

1. In all indirect methods, each sought-for quantity is obtained as a difference between two experimental weights, which results in a loss of precision. This loss may be great. Indirect methods are therefore not used except for special reasons. Also because of the loss of precision, mixtures of more than two substances are seldom analyzed indirectly, even though in theory it is possible to analyze a mixture of n components by making $n - 1$ conversions.

2. If the ratio of the equivalent weights of the original and the converted compounds for one of the sought-for elements is only slightly different from this ratio for the other element, the precision is very poor. As the difference increases, the precision becomes better. Thus, other conditions being equal, higher precision is obtained in the analysis of LiCl-KCl mixtures by the method of Ex. S1 than for NaCl-KCl mixtures. When possible, it pays to be judicious in selecting the product compounds. Thus in Ex. S1 conversion to perchlorates instead of to sulfates would give better precision.

The indirect method is generally used only in analyzing mixtures of two similar elements that are considerably different in equivalent weight, for example, Na-K, Ca-Ba, Fe-Al, Cl-Br. The indirect method is not at all appropriate for elements having similar equivalent weights, such as Co-Ni or Zn-Ni.

3. Since errors are multiplied so greatly, indirect methods are not feasible unless the conversion may be made simply, with little chance for error. Complicated conversions, involving much transfer, precipitation, washing, handling, etc., are undesirable because too many sources contribute to the over-all error, which may become large.

SUPPLEMENTARY QUESTIONS

Section 9B

S1. Describe in detail how to weigh out 1.2372 ± 0.0001 g of a stable sample. Repeat the description for 1.237 ± 0.001 g. For 1.23 ± 0.01 g.

S2. Give reasons why the method of selected sample weights is not used by students in the elementary quantitative analysis course.

S3. Under what conditions might it be feasible to use factor weights of liquid samples? Devise a technique for measuring them out. (It is easier to measure volumes than weights of liquids.)

SUPPLEMENTARY PROBLEMS

Section 9B

S1. What weight of ore should be taken in order that each 1.00 mg of Al_2O_3 obtained may represent one-tenth of a per cent of Al in the sample? *Ans.* 0.53 g.

S2. What weight of a sulfide ore should be taken in order that each gram of BaSO_4 obtained may represent ten per cent of SO_3 in the sample?

S3. What weight of Mn ore should be used in order that each milligram of $\text{Mn}_2\text{P}_2\text{O}_7$ obtained may represent one-tenth per cent of Mn? *Ans.* 0.38713 g.

S4. How many grams of an ore should be taken in order that each milligram of $\text{Mg}_2\text{P}_2\text{O}_7$ obtained may correspond to two-thousandths of a per cent of Mg in the ore?

S5. Pb may be determined electrolytically as PbO_2 . What weight of sample should be taken in order that each 1.00 mg of PbO_2 may represent two-tenths of a per cent of Pb in the sample? *Ans.* 0.433 g.

S6. What weight of sample should be taken in order that each 1.000 mg of AgCl may represent one-tenth of a per cent of Ag_2O in the sample?

S7. What weight (with an uncertainty of about 1:1000) of Fe ore should be used in order that the % Fe_3O_4 in the ore may be equal to one-fifth the number of milligrams of Fe_2O_3 obtained? *Ans.* 0.4833 g.

S8. Ore samples may contain 50–100% FeS_2 , and are analyzed by the conversion of all S to BaSO_4 , which is weighed. Select a suitable factor weight of sample, and explain specifically how to compute the % FeS_2 . The weight of BaSO_4 obtained must not be less than 0.5 g, to keep weighing errors and solubility losses low.

S9. In the analysis of rocks for silica, the latter is determined as SiO_2 . What weight of sample should be taken in order that each 0.100 g of SiO_2 may represent ten per cent of SiO_2 in the sample? That each 0.100 g may represent twenty per cent of SiO_2 in the sample? (Note the simplicity of answer where the compound sought is the same as that which is weighed.) *Ans.* 1.00 g; 0.500 g.

S10. In Prob. S9, what weight of sample should be taken in order that each 0.100 g of SiO_2 obtained may represent twenty per cent of Si in the sample?

Section 9D

S1. A 1.0000-g sample containing only Na_2SO_4 and K_2SO_4 gives a precipitate of CaSO_4 weighing 0.8637 g. What are the percentages of Na_2O and K_2O in the sample? *Ans.* 20.30% Na_2O ; 28.90% K_2O .

S2. A mixture of AgCl and AgI contains 49.82% Ag. What are the percentages of each component? What is the % Cl?

S3. A mixture containing only AgCl and AgI is heated in a current of chlorine, which converts the AgI to AgCl . If the weight loss is 27.53%, what is the % I in the mixture? *Ans.* 38.20%.

S4. Upon treatment with excess AgNO_3 , a 0.4750-g mixture containing only NaCl and NaI gives a mixture of AgCl and AgI weighing 1.0573 g. What is the % Cl in the mixture?

S5. In the manner of the section beginning on page 673, estimate the error in percentage of one component when the following indirect analyses are performed, starting in each case with 1-g samples containing 50% of each component, and assuming an error of 0.1 mg in the weight of the product.

- (a) MgCO_3 - BaCO_3 , converted to oxides.
- (b) SrCO_3 - BaCO_3 , converted to oxides.
- (c) CaCO_3 - MgCO_3 , converted to sulfates.
- (d) SrCO_3 - BaCO_3 , converted to sulfates.

Show how the answers support the statements of the text regarding the accuracy of indirect methods.

S6. By means of a numerical example, show that higher precision is obtained in Ex. S1 (p. 671) by converting to the perchlorates instead of the sulfates.

S7. A mixture containing only KCl and NaCl contains 52.34% Cl . (a) What are the percentages of K and Na in the original mixture? (b) How much KCl must be added to 100 g of this mixture to give a mixture containing 51.64% Cl ?

Ans. (a) 14.38% Na , 33.28% K ; (b) 17.16 g.

S8. A mixture containing only CaCO_3 and BaCO_3 weighs 1.1765 g. Ignition to the oxides gives a residue weighing 0.8107 g. (a) What are the % CaCO_3 and the % BaCO_3 in the original mixture? (b) What weight of sulfates would be obtained if the oxides were fumed with H_2SO_4 ?

S9. The following is a procedure for the standardization of HCl solutions. A clean, dry beaker contains an excess of primary standard-grade AgNO_3 . Beaker and AgNO_3 together weigh 29.2653 g. A 50.00-ml aliquot of the HCl to be standardized is added. The contents are then evaporated to dryness without boiling, and the residue (AgCl and AgNO_3) is dried at 120°C and weighed. If the beaker with residue weighs 29.0081 g, what is the HCl molarity? Explain the chemistry of the method. Discuss the sources of error, and the advantages and disadvantages of this method.

Ans. 0.1937 M .

S10. A method similar to that in Prob. S9 is used to standardize an H_2SO_4 solution. Compute the molarity of the H_2SO_4 solution from the following data. Weight of beaker plus excess primary standard BaCl_2 , 28.6173 g; volume of H_2SO_4 added, 50.00 ml; weight of beaker plus residue (BaSO_4 and BaCl_2) after evaporation and drying at 200°C , 28.9298 g.

S11. A 3.000-g mixture contains only BaC_2O_4 , SrC_2O_4 , and CaC_2O_4 . By controlled ignition at about 500°C , these compounds are converted to their carbonates, giving 2.5035 g of residue. Ignition of the carbonates to the oxides at high temperature gives 1.7073 g of oxides. (a) Set up the equations for computing the percentages of each of the three oxalates in the original mixture. (b) Attempt to solve these equations. (c) Explain why the solution is indeterminate.

Ans. (c) The molecular weight of SrC_2O_4 is very close to the average molecular weight of CaC_2O_4 and BaC_2O_4 . This means that a gram of pure SrC_2O_4 would give practically the same weight changes as a gram of a much different sample containing one mole of CaC_2O_4 per mole of BaC_2O_4 .

S12. In Ex. S1 (p. 671), let W_o and W_p be the respective weights of original sample and of product sulfates. (a) Express X and Y in terms of W_o , W_p , and the molecular weights of the compounds involved. (b) By the method described elsewhere in the Supplement (pp. 640-43), obtain an expression for the standard deviation (x) of X , letting w be the standard deviation of W_o and W_p . Explain how this expression supports the statements of the text regarding the accuracy of indirect methods.

ANALYSIS BY EVOLUTION. DETERMINATION OF WATER

HOW WATER IS HELD IN SOLIDS. DRYING AND DESICCANTS

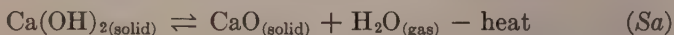
(See Sec. 10A, p. 150)

Some of the mechanisms by which water is held in solids may be described quantitatively, while others may not. In the following sections, the properties of water of constitution, water of hydration, and adsorbed water are described more fully, together with the means that may be used to liberate the water in each case.

Decomposition of $\text{Ca}(\text{OH})_2$. Solid-Gas Equilibria

(See Sec. 10A.2, p. 152)

When $\text{Ca}(\text{OH})_2$ is heated, it decomposes into CaO and H_2O . However, CaO reacts with H_2O and if the heating is carried out in a closed system so that H_2O cannot escape, an equilibrium is reached.



As long as both solid $\text{Ca}(\text{OH})_2$ and CaO are present, the pressure of H_2O exerted by the system is fixed (at a fixed temperature), and is independent of the relative amounts of the two solids. This may be understood by examining the equilibrium constant for Eq. *Sa*:

$$K = \frac{[\text{CaO}]_{(\text{solid})}[\text{H}_2\text{O}]_{(\text{gas})}}{[\text{Ca}(\text{OH})_2]_{(\text{solid})}} \quad (\text{Sb})$$

As mentioned on page 406, the concentration (or, better, activity) of a species in its pure solid state is constant and independent of the amount of solid; $[\text{CaO}]$ and $[\text{Ca}(\text{OH})_2]$ are thus constant terms. Also, the water activity, $[\text{H}_2\text{O}]$, in the gas phase is proportional to the partial pressure of H_2O ($P_{\text{H}_2\text{O}}$) in this phase. That is, $P_{\text{H}_2\text{O}} = k[\text{H}_2\text{O}]_{(\text{gas})}$. Making these substitutions in Eq. *Sb* gives

$$P_{\text{H}_2\text{O}} = \text{constant} \quad \begin{array}{l} \text{(For } \text{Ca}(\text{OH})_2\text{-CaO mixtures} \\ \text{at a fixed temperature)} \end{array} \quad (\text{Sc})$$

The particular pressure given in Eq. *Sc* is called the *equilibrium pressure*, or *decomposition pressure*. If a Ca(OH)_2 -CaO mixture is exposed to an atmosphere with $P_{\text{H}_2\text{O}}$ less than the equilibrium pressure, Ca(OH)_2 decomposes and liberates H_2O until $P_{\text{H}_2\text{O}}$ becomes equal to the decomposition pressure. If there is not enough Ca(OH)_2 in the system to bring $P_{\text{H}_2\text{O}}$ to the equilibrium value, all Ca(OH)_2 is converted to CaO and equilibrium no longer exists. Similarly, if $P_{\text{H}_2\text{O}}$ is higher than the equilibrium pressure, CaO combines with H_2O until $P_{\text{H}_2\text{O}}$ is lowered to the equilibrium value. If there is not enough CaO to do this, all CaO is converted to Ca(OH)_2 and equilibrium no longer exists.

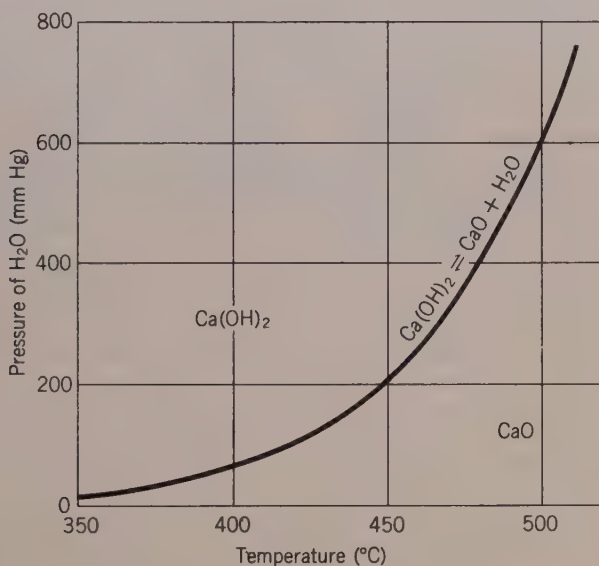


FIG. S10.1. *P-T* Diagram for Ca(OH)_2

The equilibrium $P_{\text{H}_2\text{O}}$ (Eq. *Sc*) is a function of temperature. Heat is required to decompose Ca(OH)_2 and therefore the equilibrium pressure increases with temperature, as shown in Fig. S10.1. Such a diagram, which shows the dependence of equilibrium pressure on temperature, is called a *P-T diagram*. This diagram gives the stable phases under various conditions of temperature and $P_{\text{H}_2\text{O}}$ (H_2). All points on the curve represent temperatures and water-vapor pressures at which Ca(OH)_2 and CaO may exist in equilibrium. The regions above the curve represent nonequilibrium conditions where only Ca(OH)_2 may be present, whereas in regions below the curve only CaO is present.

The equation of the equilibrium curve is derivable from theoretical principles, the slope of the curve being related to the heat of dissociation:

$$\log P_{\text{H}_2\text{O}} = \frac{-\Delta H}{2.303RT} + \text{constant} \quad (\text{Sd})$$

R is the *gas constant*, $1.987 \text{ (cal)(mole)}^{-1}(\text{deg})^{-1}$, and T is in absolute degrees. $P_{\text{H}_2\text{O}}$ is usually expressed in atmospheres, but may be expressed in any units, provided that the constant is chosen accordingly.

Thus, a plot of $\log P_{\text{H}_2\text{O}}$ against $1/T$ gives a straight line, the slope of which may be used to calculate the heat of dissociation, ΔH . A plot of the data of Fig. S10.1 gives a ΔH of 24,900 cal/mole.

The equation is of principal use in calculating heat of reaction from vapor pressure data, but it is also useful for estimates of decomposition pressures beyond the experimentally measured range.

Ca(OH)_2 decomposes if it comes into contact with an atmosphere constantly maintained at conditions below the curve of Fig. S10.1. In practice, such a decomposition may be carried out by heating a sample in a loosely covered crucible. For temperatures giving equilibrium pressures below atmospheric, the decomposition is slow, because H_2O is not lost to the air except by slow diffusion through the blanket of air above the Ca(OH)_2 in the crucible. At temperatures giving equilibrium pressures above atmospheric, the H_2O pushes back the atmosphere and flows out of the crucible, so that decomposition proceeds at a much higher rate. The temperature required to give a $P_{\text{H}_2\text{O}}$ of 760 mm (1 atm) is 511°C , which may be considered to be the minimum temperature for rapid decomposition.

If the decomposition were carried out under equilibrium conditions, an infinite time would be required. In order to make the rate of decomposition appreciable, it is necessary to heat considerably above 511°C . The higher the temperature above 511°C , the faster H_2O is lost to the atmosphere. Of course, decomposition may be brought about at a lower temperature by sweeping the H_2O out of the air space in the vessel as fast as it is formed, using an air stream of low H_2O content. Thus Ca(OH)_2 could theoretically be decomposed at 400°C by sweeping with an air stream having a $P_{\text{H}_2\text{O}}$ of less than 60 mm.

Properties of Hydrates. Vapor Pressure Diagrams

(See Sec. 10A.2, p. 152)

Study of the properties of hydrates is of extreme importance to the analytical chemist, since they have a direct bearing on (1) determination of water, (2) drying of samples and precipitates, (3) behavior of desiccants, and (4) preparation of hydrates of definite composition for use as primary standards.

Vapor pressure-composition diagrams. If a system contains two components—a soluble salt, such as BaCl_2 , and water—the equilibrium vapor pressure of water for this system depends on its composition, and

varies from zero for the pure anhydrous salt to the vapor pressure of pure water at the temperature in question. A plot of the equilibrium water-vapor pressure against composition at a given temperature is called a *vapor pressure-composition diagram* or *P-C diagram*. (It is convenient in such diagrams to express composition of the water-salt system in terms of mole percentages* rather than weight percentages.) If the salt is soluble and forms hydrates of definite chemical composition, the *P-C* curve is not uniform. As an example, BaCl_2 forms two hydrates, $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, and the *P-C* diagram at 25°C is shown in Fig. S10.2 (c5). The interpretation of this figure is given in the following paragraphs.

Pure anhydrous BaCl_2 has a $P_{\text{H}_2\text{O}}$ of zero, since it contains no water. However, as soon as a small amount of water is added, the monohydrate is formed, and an equilibrium is established.

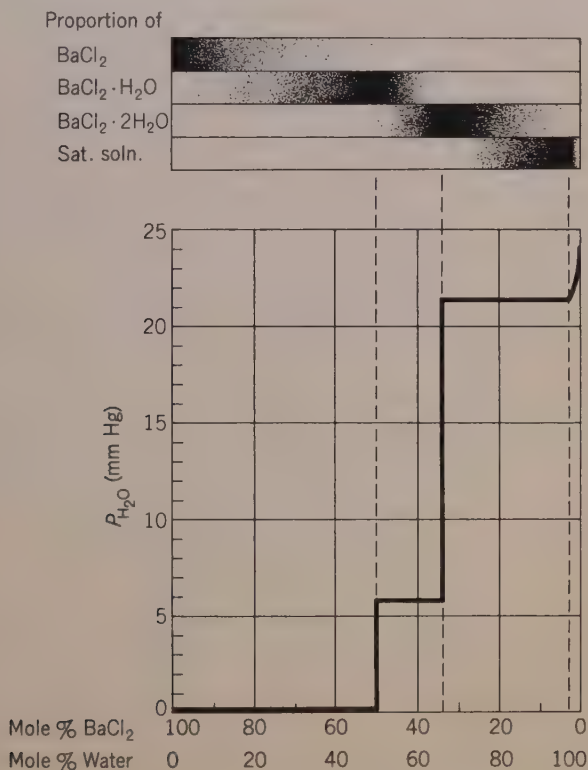


FIG. S10.2. Vapor Pressure-Composition Diagram for the System $\text{BaCl}_2\text{-H}_2\text{O}$ (25°C)

$$\text{*Mole \% of component } A = \frac{\text{moles of } A \text{ in system}}{\text{total moles in system}} \times 100$$

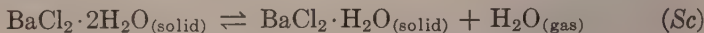


The equilibrium constant for this reaction is

$$P_{\text{H}_2\text{O}} = (\text{constant})_{0-1} \quad \begin{array}{l} \text{(For anhydrous salt-monohydrate} \\ \text{mixtures in equilibrium at con-} \\ \text{stant temperature)} \end{array} \quad (Sb)$$

The particular $P_{\text{H}_2\text{O}}$ given in Eq. *Sb* is called the equilibrium $P_{\text{H}_2\text{O}}$ of a system containing both anhydrous salt and monohydrate. As explained on page 676, the equilibrium $P_{\text{H}_2\text{O}}$ is independent of the relative amounts of the two solids as long as both are present in equilibrium. This equilibrium $P_{\text{H}_2\text{O}}$ is constant for all $\text{BaCl}_2\text{-H}_2\text{O}$ mixtures from pure BaCl_2 to pure monohydrate (i.e., from 0 to 50 mole % water). From Fig. S10.2, this equilibrium $P_{\text{H}_2\text{O}}$ is 0.2 mm at 25°C.

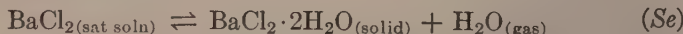
As water is added to the anhydrous salt, an increasing proportion of the BaCl_2 is converted to the monohydrate phase. All anhydrous salt disappears after enough water is added to give exactly 50 mole % water, which is the composition of the monohydrate. The conversion of the anhydrous phase to the monohydrate is depicted in the strip diagram at the top of Fig. S10.2. Addition of a little more water than this causes formation of some dihydrate, and a new equilibrium is established.



$$P_{\text{H}_2\text{O}} = (\text{constant})_{1-2} \quad \begin{array}{l} \text{(For monohydrate-dihydrate mix-} \\ \text{tures in equilibrium at constant} \\ \text{temperature)} \end{array} \quad (Sd)$$

The new equilibrium pressure (5.7 mm at 25°C, from Fig. S10.2) is constant for all mixtures from pure monohydrate to pure dihydrate (i.e., 50–66.7 mole % water).

As water is added above 66.7 mole % no higher hydrates are formed, but the dihydrate dissolves to give the saturated solution, and a third equilibrium is established.



$$P_{\text{H}_2\text{O}} = (\text{constant})_{2-\text{sat soln}} \quad \begin{array}{l} \text{(For dihydrate-saturated solution} \\ \text{mixtures in equilibrium at con-} \\ \text{stant temperature)} \end{array} \quad (Sf)$$

The equilibrium $P_{\text{H}_2\text{O}}$ established is that of the saturated solution and is constant (21.4 mm) for all mixtures from pure dihydrate to pure saturated solution (i.e., 66.7–96.9 mole % water). As water is added above 66.7 mole %, more dihydrate dissolves to form saturated solution, the proportion of which increases in the system. When 96.9 mole % water is added, all dihydrate disappears and only saturated solution exists. As more water is added to the saturated solution, it becomes diluted, and the $P_{\text{H}_2\text{O}}$ of the solution increases uniformly with dilution, approaching the $P_{\text{H}_2\text{O}}$ for pure water (23.8 mm) as the solution becomes infinitely dilute.

The P - C diagram may be used to predict the resultant composition of a water-salt system that is placed in contact with an atmosphere having a certain $P_{\text{H}_2\text{O}}$. In general, the system with the higher $P_{\text{H}_2\text{O}}$ gives up water to the system with the lower $P_{\text{H}_2\text{O}}$, until an equilibrium is attained for which the water-vapor pressures of both systems are the same.

It should be mentioned that Fig. S10.2 is an idealized diagram, which assumes water retention by no mechanism other than hydrate formation. Owing to adsorption of water by the solids, the corners are rounded, and the steep parts are not absolutely vertical.

P - T diagrams. The equilibrium $P_{\text{H}_2\text{O}}$ for each equilibrium (Eqs. S_a , S_c , S_e) increases with temperature, and the location and shape of the curve in Fig. S10.2 vary with temperature. To show how the equilibrium $P_{\text{H}_2\text{O}}$ of each equilibrium system depends upon temperature, a series of plots is required. Figure S10.3 is such a *vapor pressure-temperature diagram*, or P - T diagram for the BaCl_2 -water system (C5). (The diagram is not accurate, since data are fragmentary.)

Study of Fig. S10.3 shows that the equilibrium $P_{\text{H}_2\text{O}}$ increases exponentially with temperature, just as does the equilibrium $P_{\text{H}_2\text{O}}$ for $\text{Ca}(\text{OH})_2$. Points on the curves represent the only conditions for which the designated substances may exist in equilibrium. All other points

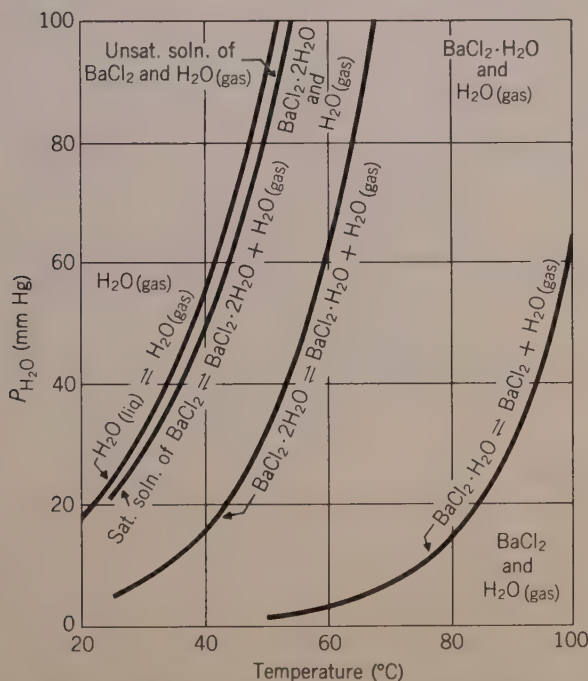


FIG. S10.3. Vapor Pressure-Temperature Diagram for the System BaCl_2 - H_2O

(between curves) represent nonequilibrium conditions, under which only the designated substances may exist. Thus if a mixture of BaCl_2 and $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ is put in a closed system and heated, the bottom curve represents $P_{\text{H}_2\text{O}}$ of the system as a function of temperature, as long as both anhydrous salt and monohydrate are present.

Preparation of hydrates. It is occasionally necessary to prepare pure hydrates of known composition, so that they may be used as primary standard substances. Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and oxalic acid ($\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) are two such standards. After crystallization the hydrate contains excess water, which may be removed by equilibrating the substance to an atmosphere with a $P_{\text{H}_2\text{O}}$ in which only the desired hydrate is stable. The beginning sample may also be the anhydrous salt, which can be brought up to the desired composition by the correct atmospheric conditions.

For example, to prepare a sample of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ at 25°C it is necessary to use an atmosphere with $P_{\text{H}_2\text{O}}$ between the limits 5.7 and 21.4 mm (Fig. S10.2). If a $P_{\text{H}_2\text{O}}$ of 21.4 mm or greater is used, excess water remains in the sample; if a $P_{\text{H}_2\text{O}}$ of 5.7 or less is used, the sample may be deficient in water. In actual practice, the choice of the equilibrating $P_{\text{H}_2\text{O}}$ is not quite so wide as may be implied from a diagram like Fig. S10.2, for the steep parts of the curve are not strictly vertical.

To prepare small quantities of a hydrate in the laboratory, the salt may be placed in a desiccator filled with another water-salt system having an equilibrium $P_{\text{H}_2\text{O}}$ within the desired range. A desiccator so used is called a *hydrostat*. To increase the rate of equilibration, the sample should be powdered and spread on a watch glass. A vacuum desiccator is also useful for increasing the rate of equilibration. Powdering also reduces retention of occluded water. In another method, suitable for larger quantities, a stream of gas that has been previously brought to the desired $P_{\text{H}_2\text{O}}$ is passed through the sample. The gas stream may be equilibrated to the desired $P_{\text{H}_2\text{O}}$ by bubbling it through water maintained at a particular temperature.

Table S10.1 gives the equilibrium $P_{\text{H}_2\text{O}}$'s of various systems used in hydrostats.

Adsorbed Water

(See Sec. 10A.1, p. 151)

A gas is adsorbed upon a solid if the concentration of the gas is higher in the immediate vicinity of the solid than it is in the bulk of the gas phase. The solid substance is called the *adsorbent* and the adsorbed substance is called the *adsorbate*. The adsorbate molecules may be held to the adsorbent surface principally by three types of forces: van der Waals, corresponding to physical adsorption, and chemical forces, corre-

TABLE S10.1

WATER-VAPOR PRESSURE OF AQUEOUS SYSTEMS AT VARIOUS TEMPERATURES*

MIXTURE	P_{H_2O} AT VARIOUS TEMPERATURES (MM)†				
	10°C	15°C	20°C	25°C	30°C
MgCl ₂ —MgCl ₂ ·2H ₂ O.....			0.009		
KOH—KOH·H ₂ O.....					0.6
CaCl ₂ —CaCl ₂ ·H ₂ O.....			0.26		
CaCl ₂ ·H ₂ O—CaCl ₂ ·2H ₂ O.....		0.6			
NaOH—NaOH·H ₂ O.....			0.5		
K ₂ CO ₃ —K ₂ CO ₃ ·2H ₂ O.....				1.2	
KOH—sat. soln.....			0.9		
NaOH—sat. soln.....			1.0		
NaI—NaI·2H ₂ O.....		1.5	2.3	3.3	4.8
CaBr ₂ ·6H ₂ O—sat. soln.....	2.1	2.7	3.3	4.1	4.8
CaCl ₂ ·2H ₂ O—CaCl ₂ ·6H ₂ O.....	1.9	2.7	3.9	5.2	7.3
Na ₂ HPO ₄ —Na ₂ HPO ₄ ·2H ₂ O.....		3.5	4.9	6.9	
CaCl ₂ ·6H ₂ O—sat. soln.....	3.5	4.5	5.8	6.9	8.3
NaBr—NaBr·2H ₂ O.....	2.8	4.1	6.0	8.6	12.1
K ₂ CO ₃ ·2H ₂ O—sat. soln.....			7.7	10.7	
Ca(NO ₃) ₂ ·4H ₂ O—sat. soln.....	6.0	7.7	9.6	11.9	14.3
Na ₂ HPO ₄ ·2H ₂ O—Na ₂ HPO ₄ ·7H ₂ O.....	4.6	6.8	9.8	14.0	19.7
NaBr·2H ₂ O—sat. soln.....	5.8	7.8	10.3	13.6	17.5
NH ₄ NO ₃ —sat. soln.....	6.3	8.4	11.0	14.3	18.1
Na ₂ CO ₃ ·H ₂ O—Na ₂ CO ₃ ·10H ₂ O.....	6.1	8.8	12.6	18.1	
Na ₂ HPO ₄ ·7H ₂ O—Na ₂ HPO ₄ ·12H ₂ O.....	6.0	8.9	13.1	19.3	
Na ₂ SO ₄ —Na ₂ SO ₄ ·10H ₂ O.....	6.3	9.2	13.3	19.0	
Na ₂ SO ₄ ·10H ₂ O—sat. soln.....		12.2	15.7	20.2	24.8
Na ₂ CO ₃ ·10H ₂ O—sat. soln.....			15.9	21.2	27.6
KNO ₃ —sat. soln.....			16.6	22.4	29.9
Water.....	9.2	12.8	17.5	23.8	31.8

* Data taken from I. M. Kolthoff and E. B. Sandell, *Textbook of Quantitative Inorganic Analysis*, 3d ed. (New York: Macmillan, 1952), Tables 25 and 26, with permission of the publisher.

† In the table, P_{H_2O} is expressed absolutely, in millimeters of Hg. P_{H_2O} is often expressed on a relative basis, as relative humidity (r.h.), defined as

$$\frac{\text{Actual } P_{H_2O} \text{ at temperature, } t}{\text{Saturation } P_{H_2O} \text{ at temperature, } t}$$

The saturation P_{H_2O} is that in equilibrium with pure water, shown in the bottom line of the table. Thus a P_{H_2O} of 7.1 mm at 10°C would be equivalent to an r.h. of $7.1/9.2 = 0.77$, or 77%.

sponding to chemisorption. Electrostatic forces are also important in some systems, particularly in the adsorption of ions from solution.

There are several fundamental differences between physical and chemical adsorption, due mainly to the differences in strength of binding between the adsorbent and adsorbate. These differences manifest themselves in the ease with which adsorption and desorption occur:

1. The strength of binding for physical adsorption is usually much less than for chemisorption. The heat of adsorption for a physically held adsorbate is of the same order as its heat of vaporization—of the order of a few kilocalories per mole for most substances. For chemisorbed substances, however, heats of adsorption range from tens to hundreds of kilocalories per mole—comparable to heats of chemical reactions.

2. The van der Waals forces that operate in physical adsorption are longer in range and quite unspecific compared to the short-range and specific binding forces that come into play in chemisorption. Thus, the extent of physical adsorption depends little upon the structure of the adsorbate, but is generally greater the higher the boiling point of the adsorbate. On the other hand, the extent of chemisorption is entirely dependent upon the nature and chemical structure of the adsorbate and adsorbent.

3. At a fixed temperature, the extent of adsorption is a function of the vapor pressure of the adsorbate. A plot of extent of adsorption versus vapor pressure is called an *adsorption isotherm*. Figure S10.4 shows the five different types of adsorption isotherms that are observed (B27). Examples of all five types may be found in physical adsorption, but chemisorbed systems follow only Type I dependence.

The qualitative interpretation of the isotherms of Fig. S10.4 is that the adsorbate goes on as a monolayer up to the first flat region. A rapid rise in the isotherm after the first flat region represents the formation of multilayers of adsorbed molecules. A second flat region, which may

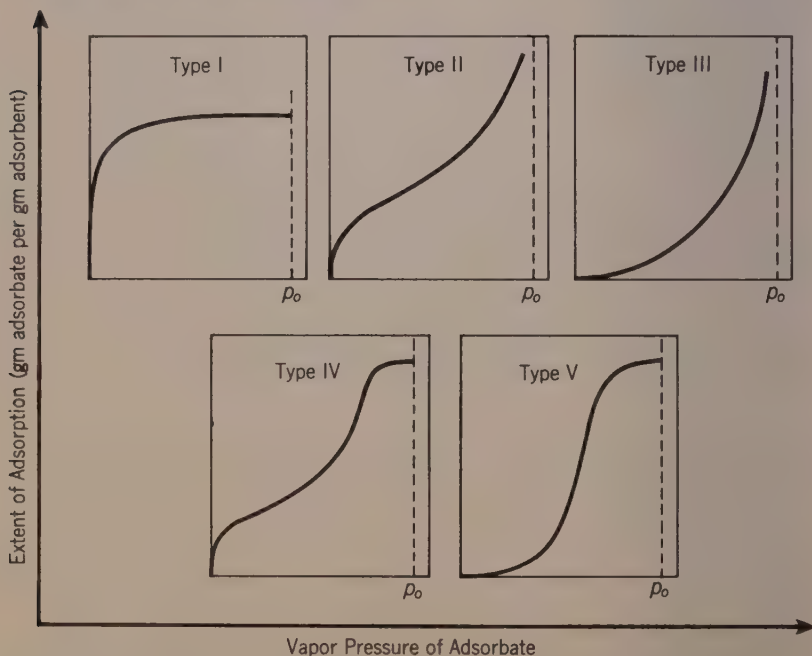


FIG. S10.4. The Five Isotherm Types Observed in Adsorption— p_0 is the vapor pressure of the pure adsorbate. (Reprinted from S. Brunauer, *Physical Adsorption*, Vol I [Princeton: Princeton University Press, 1943], Fig. 68, by permission of the publisher.)

occur as saturation is approached, represents condensation of the adsorbate in the capillaries of the adsorbent (see Prob. S21, p. 699).

Several types of mathematical equations may be used to represent the isotherms of Fig. S10.4. The Freundlich, Langmuir, and the Brunauer-Emmett-Teller equations are most often used. Mysels gives an excellent elementary comparison of the three equations (M25). For purposes of this text, however, a quantitative description of the isotherms is not necessary.

The behavior of adsorbed water is more complicated than that of less condensible substances. On most adsorbents, water is chemisorbed at least in part. Water follows all five types of isotherms. Water on many oxides and silica gel follows a Type I isotherm. On asbestos fibers, water shows a Type II isotherm. Type III behavior is shown on glass, Type IV on CuO and Fe₂O₃, and Type V on charcoal.

Because of the steepness of the isotherm at low vapor pressures, it may be very difficult to remove the last traces of water from Type I, II, or IV systems, whereas Type III or V systems may be very easy to dry.

Heat is invariably liberated in the adsorption process, and the extent of adsorption decreases as the temperature increases.* In physical adsorption, the extent of adsorption diminishes only moderately as temperature increases, because of the low heat of adsorption. Chemisorbed systems with high heats of adsorption have high temperature coefficients.

4. Physical adsorption is usually rapid. (Sometimes, when deep pores or narrow capillaries in the adsorbent must be penetrated, the rate is low.) However, the chemical reactions that accompany chemisorption often have considerable activation energies and correspondingly low reaction rates.

The rate of physical adsorption usually increases moderately with temperature, the increase being explainable by the increase in rate of diffusion of the adsorbate through pores and capillaries to the adsorption sites in the adsorbent. Because of the exponential dependence of rate on temperature, the rate of a chemisorption process may increase very rapidly with temperature.

5. A physically adsorbed substance can be desorbed without alteration. On the other hand, chemisorption is often nonreversible. It may not only be difficult to desorb the adsorbate, but the desorbed substance may be different from the originally adsorbed substance. Thus, oxygen chemisorbed on charcoal cannot be removed as such; desorption yields CO₂ and CO.

*Some apparent contradictions of this statement in complicated systems are due to simultaneous operation of more than one type of adsorption process.

Drying

(See Secs. 8C, p. 103, and 10B.1, p. 153)

The means used to drive water out of a sample depend on the way in which the water is held and on the stability of the sample. Fundamentally, there are several methods of drying substances.

A simple procedure is to heat the sample until its $P_{\text{H}_2\text{O}}$ is greater than that of the atmosphere, so that the sample loses water to the atmosphere. This method is fast, and is used whenever the stability of the sample permits.

If the $P_{\text{H}_2\text{O}}$ of the air is within the $P_{\text{H}_2\text{O}}$ range of the dried product, the sample may be dried by evaporation in air. This procedure is often used for substances unstable to heat. For example, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ may be prepared by the air-drying of wet samples. Examination of Fig. S10.2 shows that the dihydrate may be prepared by drying at 25°C in an atmosphere with a $P_{\text{H}_2\text{O}}$ in the range 5.7–21.4 mm. So long as the air has a $P_{\text{H}_2\text{O}}$ in this range (a relative humidity of 24–90%), it is suitable for drying.

If the $P_{\text{H}_2\text{O}}$ of the atmosphere is above the $P_{\text{H}_2\text{O}}$ range of the dried product, and if the sample is unstable to heat, it may be dried in an air stream that has been treated to reduce its $P_{\text{H}_2\text{O}}$ to that of the desired product. For substances unstable in air, an inert gas stream may be used.

Desiccants

(See Sec. 8C.3, p. 106)

Any stable solid or liquid substance with the following properties may be used as a desiccant. (1) The equilibrium $P_{\text{H}_2\text{O}}$ of the desiccant and its first hydrated form should be low. (2) The desiccant should have a good capacity; that is, it should be able to absorb a rather high percentage of its own weight of water without much increase in $P_{\text{H}_2\text{O}}$. (3) The desiccant should absorb water rapidly.

Some desiccants may take on water as water of hydration or constitution. However, a few of the most important desiccants (SiO_2 , Al_2O_3) remove water primarily by adsorption. Table S10.2 lists the relative efficiencies of certain samples of some common desiccants. To determine each figure in the table, moist air was swept through a U-tube filled with the desiccant, and the water content of the effluent stream was measured when it reached a steady state (but before the desiccant was exhausted). The figures of Table S10.2 tell nothing about the capacities of the desiccants (B22, S20).

While the order in Table S10.2 undoubtedly represents the order of drying efficiencies for the particular samples that were investigated, each figure for residual water should not be interpreted to have quantitative

TABLE S10.2

RELATIVE EFFICIENCIES OF DRYING AGENTS AT 30°C*

MATERIAL	RESIDUAL WATER IN EFFLUENT STREAM	
	Milligrams per Liter	P_{H_2O} (Millimeters of Hg)
P_2O_5	None	None
BaO.....	0.0007	0.0007
$Mg(ClO_4)_2$ (anhydrous) "Anhydron".....	0.002†	0.002†
CaO (C.P., powdered).....	0.003	0.003
$CaSO_4$ (anhydrous) "Anhydrite".....	0.005	0.005
Al_2O_3 (anhydrous) "Hydralo".....	0.005	0.005
KOH (U.S.P., sticks).....	0.014	0.014
Silica gel.....	0.03	0.03
$Mg(ClO_4)_2 \cdot 3H_2O$ "Dehydrite".....	0.031	0.033
$CaCl_2$ (anhydrous).....	0.36	0.38
NaOH (C.P., sticks).....	0.80	0.84
$Ba(ClO_4)_2$ (anhydrous) "Desicchlora".....	0.82	0.86
$ZnCl_2$ (C.P., sticks).....	0.98	1.03
$CaCl_2 \cdot 0.25H_2O$ (technical anhydrous).....	1.25	1.31
$CaCl_2 \cdot H_2O$ (granular anhydrous).....	1.5	1.6

* Data taken in part from J. H. Bower, *Journal of Research of the National Bureau of Standards*, 12, 241 (1934), Table 1, with permission of the publisher.

† Probably high.

significance for other samples having the same chemical composition. For any particular chemical substance, the drying efficiency is not simply related to the equilibrium P_{H_2O} of the substance alone. The drying efficiency may depend greatly upon other physical properties that determine the rate of water removal, such as surface nature, which is determined by the mode of preparation and preliminary treatment of the substance. Thus fused quartz is anhydrous silica, but it possesses virtually no desiccating power. On the other hand, some preparations of well-activated** silica gel may be better than that listed in Table S10.2 by factors as high as 50, and may be better than anhydrous $CaSO_4$ and activated alumina with respect to both the residual water and total capacity. Different preparations of anhydrous alumina show similar wide variations in drying efficiency, and to a lesser extent KOH, $CaSO_4$, $CaCl_2$, and other desiccants seem to show such variations also.

P_2O_5 is the most efficient drying agent known. On absorbing water,

**Activation ordinarily consists simply of heating in a stream of dry air. Several substances, including silica gel, activated alumina, anhydrous $CaSO_4$, and $Mg(ClO_4)_2$ may be used again and again as desiccants, with alternating periods of reactivation. The drying efficiency after reactivation depends both on the initial character of the agent and on the temperature and dryness of the air during activation. For long life, it is best not to activate at a temperature higher than that necessary to produce the desired drying efficiency.

it forms a syrupy sheet of phosphoric acid, which reduces the rate of drying and which must be removed occasionally. BaO must be prepared to give a porous product, or drying capacity and rate are poor. Anhydrous is a very efficient desiccant which may be regenerated simply by being heated to drive off the water. CaCl_2 is really not a good drying agent, but it is often adequate to maintain a "dry" atmosphere in the desiccator. Concentrated H_2SO_4 (about 5% water) also falls in this class. To prevent splashing when H_2SO_4 is used in the desiccator, glass beads should be added until the bead level is slightly above the liquid level. H_2SO_4 darkens after long use, owing to reaction with organic matter (dust), and SO_2 is slowly liberated. It is not generally recommended.

OTHER METHODS FOR DETERMINING WATER

(See Sec. 10B, p. 152)

Since the determination of water in virtually all types of materials is so important and frequent, a myriad of methods has been developed. An excellent review has been written by Michell (M19). Following are a few of the more important procedures, chosen to stress the variety of principles on which a quantitative analysis may be based.

Distillation Method

The sample is distilled with an excess of a liquid having a boiling point higher than water and immiscible with it. Xylene and toluene are frequently used. Upon distillation the liquid with the higher boiling point carries the water quantitatively. The vapors are condensed (as two phases), and the volume of water in the distillate is measured. The distillation procedure is sometimes used on samples that cannot be oven-dried. Because of the relatively low temperatures employed there is often less decomposition than for oven-drying. Distillation is successful for determining the water content of cereals, fats, oils, and other food-stuffs, as well as plant materials.

Small Amounts of Moisture in Organic Substances

The water content may be very low in some samples, and the loss-in-weight and absorption methods are not applicable. The two following methods are among several that may be used.

Turbidity method. Occasionally, small amounts (0.1–1%) of water must be determined in liquids in which the water is quite soluble (ethanol, glacial acetic acid, acetone, etc.). On mixing such a liquid with, say, an equal volume of a nonpolar one, such as a paraffin oil, the water is made insoluble, and the solution becomes turbid. The solubility of

the water in the resulting solution may be increased by heating, and if the solution is heated sufficiently, the turbidity disappears. The temperature at which the turbidity disappears is a measure of the water content of the original liquid, which may be found by reference to a working curve of temperature required for disappearance of turbidity plotted against % water in the original liquid. The working curve is prepared by running a few samples containing known amounts of water.

Karl Fischer titration. Water in an organic liquid is titrated with a standard solution of iodine in methanol containing excess SO_2 and pyridine to an end point marked by the first permanent appearance of the brown color of iodine.



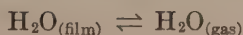
This method is applicable to more types of samples than any other method for determining water. Both organic and inorganic samples may be analyzed. There are interfering compounds that also react with the reagent, but methods exist to eliminate some of these. Water in solid samples may be determined after extraction into an inert solvent (e.g., methanol, etc.), or after distillation with an inert solvent that carries the water. As little as 0.2 mg of water may be detected.

There are many details in this procedure that have been omitted from this discussion. For example, the mechanism of the reaction is more complicated than is indicated by the equation; pyridine is involved. Also, the method is so sensitive that reagents must be stored and used out of contact with the atmosphere, which contaminates the sample and reagents with significant amounts of water.

Instrumental Methods for Determining Moisture in a Gas Stream

The vapor pressure of water in a gas stream may be found by measuring the *dew point*, which is the temperature at which water condenses out of the gas phase. Many different experimental arrangements are described in the literature. One is a completely automatic device that gives a continuous record of the $P_{\text{H}_2\text{O}}$. The gas stream is passed over a temperature-controlled mirror surface, from which a light beam is reflected into a photocell. When the mirror temperature reaches the dew point, condensation on the mirror scatters the light, and greatly reduces the intensity of the reflected beam. The temperature of the mirror at this point is automatically recorded and taken as a measure of the $P_{\text{H}_2\text{O}}$.

A continuous record of $P_{\text{H}_2\text{O}}$ in a gas stream may be obtained by passing the stream over a film of $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ on a nonconducting base. The film comes rapidly into equilibrium with the gas stream.



The greater the $P_{\text{H}_2\text{O}}$, the greater are the water content and the conductivity of the film. (Conc. $\text{H}_2\text{SO}_4\text{-H}_3\text{PO}_4$ is a poor conductor, but the addition of a small amount of water causes ionization and an increase in conductance.) The conductivity of the film is automatically and continuously recorded and taken as a measure of the water content.

In another method, the water is absorbed in a P_2O_5 film, as above, but is electrolyzed. The $P_{\text{H}_2\text{O}}$ of the gas stream determines the water content of the film, which in turn determines the magnitude of the electrolysis current. The current is recorded continuously and taken as a measure of $P_{\text{H}_2\text{O}}$ in the gas stream.

Water has a considerably higher dielectric constant than most non-aqueous substances. Water in all sorts of solids and liquids may be measured by placing the sample in the field of a capacitor which determines the frequency of a high-frequency oscillator. Water in the sample affects the capacitance, which in turn affects the frequency of the oscillator. The frequency is observed and taken as a measure of the water content of the material.

Commercial versions of all of these instruments are available.

OTHER EVOLUTION METHODS OF ANALYSIS

(See Sec. 10C, p. 155)

Thermal Decomposition of CaCO_3

Most carbonates may be decomposed by heating. Figure S10.5 is a P - T diagram for the decomposition of CaCO_3 (U7):



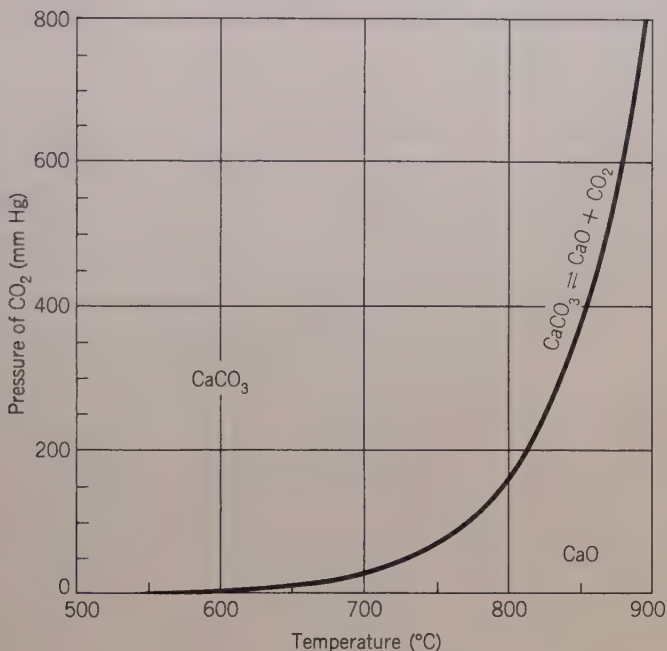
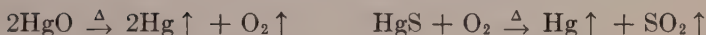
According to the principles on page 676, the equilibrium constant for this reaction is

$$P_{\text{CO}_2} = \text{constant} \quad \text{(For CaO-CaCO}_3 \text{ mixtures at a fixed temperature)}$$

From Fig. S10.5, the temperature required for a decomposition pressure of 1 atmosphere is 895°C . The decomposition of limestones, whose carbonates are principally CaCO_3 and MgCO_3 , is carried out at temperatures between 900 and 1000°C . The data of Fig. S10.5 is also useful in determining the temperature at which CaCO_3 preparations may be dried in air without decomposition. (See Prob. S3, p. 700.)

Determination of Hg in an Ore

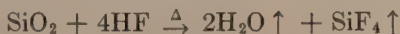
Most Hg compounds are completely decomposed when heated to about 500°C in air. The principal compounds present in ores are HgO and HgS , which behave as follows:

FIG. S10.5. *P-T* Diagram for CaCO₃

It is not possible to determine Hg by a loss-in-weight procedure, for substances other than Hg are also evolved. However, the Hg evolved may be collected by amalgamation on a previously weighed plate of Au, Ag, or Cu, which is cooled and held over the mouth of the decomposition vessel. Deposition of interfering substances along with Hg causes error unless provided for by methods that are described in the literature (S9).

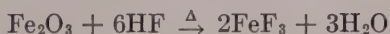
Determination of SiO₂ by Conversion to SiF₄

In the determination of Si (as silicates in rocks, etc.) the Si is usually obtained for weighing as SiO₂. However, before it is precipitated the SiO₂ passes through a colloidal stage, and has a great tendency to become contaminated, principally with Fe₂O₃ and Al₂O₃. The SiO₂ may be separated by volatilization as SiF₄ from such nonvolatile impurities by evaporation with an excess of HF.

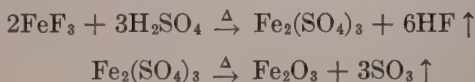


Since all the products and the excess reagent HF are volatile, the loss in weight of the sample represents the SiO₂.

Error may result from partial conversion of the oxide impurities to the fluorides.

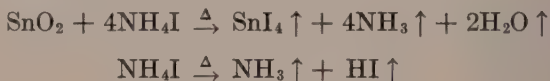


A mixture of HF and H₂SO₄ prevents this error; the HF evaporates first and leaves H₂SO₄, which metathesizes any metallic fluorides into the sulfates. The sulfates decompose to the oxides upon ignition, and the impurities are therefore left in the same form in which they existed before volatilization with HF (S9).



Determination of SnO₂ by Conversion to SnI₄

Sn is usually separated from other metals by precipitation from acid solution as hydrous SnO₂, which is dried by ignition to SnO₂ for weighing. The hydrous SnO₂ is a colloidal precipitate and has a great tendency to coprecipitate other metallic ions that may be present (e.g., Cu, Fe). No matter how much care is used, the precipitated SnO₂ is contaminated with the other oxides. Error due to such contamination may be avoided by filtering, drying, and weighing the precipitate, and then heating it with NH₄I at 425–475°C. The SnO₂ is volatilized as SnI₄, and excess NH₄I also volatilizes (S9).



The SnO₂ is found as the weight loss on such treatment. Any other oxides which may be partially converted to nonvolatile iodides are reconverted to the oxides by ignition after evaporation with conc. HNO₃.

The Thermobalance

In the ordinary evolution procedure the sample is heated to constant weight for a fixed time at a certain temperature. This procedure lacks selectivity, for it is only rarely possible to choose a temperature at which the sought-for compound decomposes at a good rate and at which other compounds that may be present remain stable.

The thermobalance extends the applicability, accuracy, and selectivity of the evolution method. Basically, the thermobalance is a suspension balance associated with a furnace, and gives a continuous record of the weight of a sample while it is being heated in the furnace. Ignitions may therefore be performed by raising the temperature in any desired way—usually slowly and uniformly, by automatic control. It

is not necessary to cool and preserve a stable form of the ignited sample for weighing at room temperature; and so a multitude of errors associated with classical gravimetric methods is avoided.

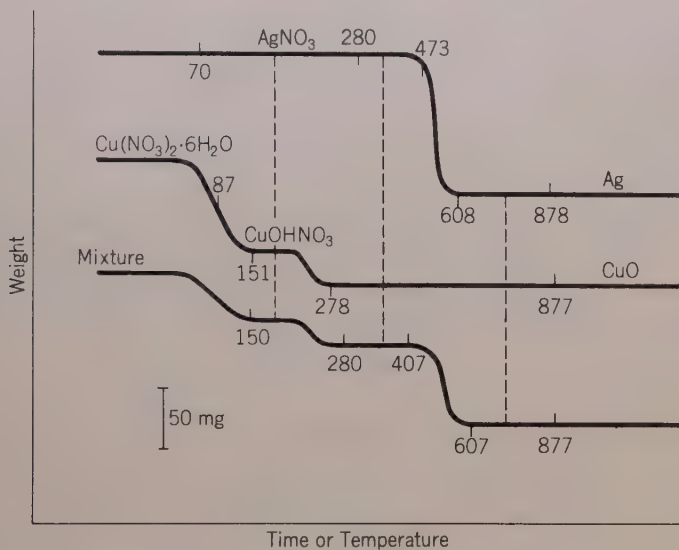


FIG. S10.6. Decomposition of Silver and Copper Nitrates on the Thermobalance (Reprinted from C. Duval, *Analytical Chemistry*, 23, 1271 [1951], Fig. 73, by permission of the publisher.)

Figure S10.6 shows weight versus time (i.e., temperature) curves for AgNO_3 and $\text{Cu}(\text{NO}_3)_2$, singly and in a mixture. Such curves are called *pyrolysis curves*. The temperatures attained are annotated in centigrade degrees on the curves. The stable compounds formed in the various horizontal (constant weight) regions are also annotated on the curves. It may be seen that AgNO_3 is stable up to about 470° and then decomposes to Ag , which is stable above 608° . On the other hand, $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ is stable only around room temperature; above 58° it decomposes to CuOHNO_3 , which is stable from about 150° to 200° . Above 200° CuOHNO_3 decomposes to CuO , which is stable above 278° . When a mixture of the nitrates is heated, the weight losses at various temperatures permit calculation of the amount of each compound in the mixture. It is therefore possible to determine Ag and Cu in their binary alloys. Relative errors are about 0.3%. Many other compounds behave similarly and may be determined in a similar manner (Probs. S7–S9, p. 700), by automated procedures requiring only a minimum of the operator's attention.

The thermobalance has much wider uses than just for routine gravimetric analysis. It is an extremely valuable and versatile research in-

strument. In particular, it is employed for (1) study of the behavior of substances when heated, (2) determination of the proper conditions at which a gravimetric precipitate or primary standard preparation must be heated to acquire a stoichiometric composition, (3) discovery of new compounds stable only at elevated temperatures.

Many methods of determination based on new weighing forms are possible with the thermobalance that are not possible by classical gravimetric procedure. The thermobalance has permitted establishment of conditions for the preparation and drying of precipitates and primary standard substances more precisely than has heretofore been possible.

Duval (D12, D13) describes studies on the gravimetric determination of most elements. A recent symposium provides references to much work in the decade 1950–60 (A9). Included are papers on modifications of equipment, and also on the method of differential thermal analysis.

PREPARATION OF STUDENT SAMPLES

(See Exp. 10.1, p. 156)

Barium chloride dihydrate is stable over a moderate range of relative humidity (p. 679), and a series of $\text{NaCl} \cdot \text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ samples may be prepared for unknowns in Exp. 10.1. A suitable series might contain about twenty members in the range 90–100% of dihydrate, each member separated by about 0.06% H_2O from its nearest neighbors. With such a series, a student may be informed of the correct composition of his sample after he makes his report, without invalidating future use of the sample for other students.

Each sample in the series may be prepared by mixing carefully weighed amounts of reagent-grade $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ and NaCl , and mixing thoroughly. The composition of each sample is calculated from the weights of reagent-grade chemicals used. It is not necessary to analyze individual members of the series, but spot checks on a few members may be made if desired.

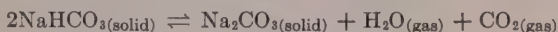
An adequate procedure for making up series members in approximately kilogram lots is as follows: (1) Sieve the powdered reagent-grade chemicals, retaining the fractions that pass the 100-mesh screen. (2) Dry the NaCl overnight at 150°C . Expose the $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ to air at 30–80% relative humidity for several days. Thereafter, keep the storage bottles securely capped or stoppered. (3) On an oversize balance, weigh out the proper amounts of NaCl and of dihydrate to the nearest 0.01 g into a good mixer and mix thoroughly. A V-type blender (Patterson-Kelly Co., East Stroudsburg, Pennsylvania) gives adequate mixing in 2–3 hours. (4) After mixing a batch, it should be bottled into vials of a size suitable for individual student samples. Immediate

bottling into student-sized samples eliminates error due to segregation that may occur in larger storage bottles, due to settling or caking over a long period of time. The vials should be securely capped, since the relative humidity will at times fluctuate outside the range 30–80%. To reduce errors and mix-ups in dispensing, it is desirable that all of the vials be numbered with the sample number, which should of course be removed just prior to issuance.

SUPPLEMENTARY QUESTIONS

Sections 10A, B

S1. Write the simplest forms of the equilibrium constants for each of the following reactions:



S2. Explain why $\text{Ca}(\text{OH})_2$ does not decompose very rapidly in a covered crucible at 500°C . How could the decomposition be hastened at this temperature?

S3. How may $\text{Ca}(\text{OH})_2$ be maintained without decomposition at 505°C ?

S4. What would be the minimum temperature required for the decomposition of $\text{Ca}(\text{OH})_2$ in contact with a gas stream having a $P_{\text{H}_2\text{O}}$ of 20 mm of Hg?

S5. Is it correct to speak of 5.7 mm as being the vapor pressure of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ at 25°C ? Over what range of $P_{\text{H}_2\text{O}}$ is this dihydrate stable at 25°C ?

S6. Describe what happens when a large volume of air ($P_{\text{H}_2\text{O}} = 22.0$ mm) is passed through a small amount of anhydrous BaCl_2 at 25°C . What happens if the $P_{\text{H}_2\text{O}}$ in the air is 10.0 mm? 4.0 mm?

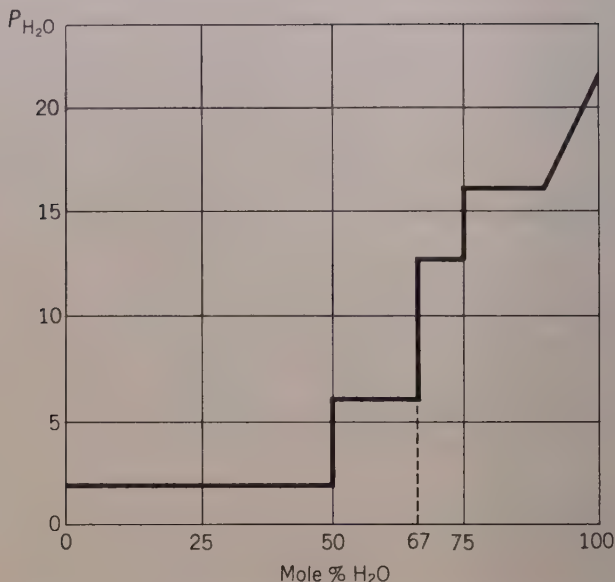
S7. What phases are present in BaCl_2 -water systems that have the following $P_{\text{H}_2\text{O}}$ at 40°C : 80, 56 (on curve of Fig. S10.3, p. 681), 52, 50 (on curve), 30, 16 (on curve), 10, 0.01 mm?

S8. A system containing only $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ at 35°C is in stable equilibrium with an influent gas stream having a $P_{\text{H}_2\text{O}}$ equal to 10.0 mm. (a) What happens if the system cools to 25°C , and the gas stream continues with the influent $P_{\text{H}_2\text{O}}$ unchanged? What is the $P_{\text{H}_2\text{O}}$ in the first portions of the effluent stream after the temperature change occurs? (b) Answer part a if the temperature drops to 10°C . Is equilibrium ever attained between the gas stream and the BaCl_2 -water system?

S9. Explain the following statements, using Fig. S10.2 (p. 679). (a) If a relatively large amount of a BaCl_2 -water system comes in contact with a relatively small amount of a dry atmosphere, the equilibrium $P_{\text{H}_2\text{O}}$ of the BaCl_2 -water system is established without appreciable change in the latter's composition. (b) If a small amount of a BaCl_2 -water system is swept with a large volume of a gas stream having a certain $P_{\text{H}_2\text{O}}$, the composition of the BaCl_2 -water system changes until its equilibrium $P_{\text{H}_2\text{O}}$ becomes equal to that of the gas stream. (c) If a BaCl_2 -water system having a certain equilibrium $P_{\text{H}_2\text{O}}$ comes in contact with a volume of gas having about the same amount of water, but a different $P_{\text{H}_2\text{O}}$, the final $P_{\text{H}_2\text{O}}$ will be intermediate between the two original ones.

S10. Draw qualitatively the vapor pressure-composition diagram for a water-salt (MCl_2) system that forms the hydrates: $\text{MCl}_2 \cdot \text{H}_2\text{O}$, $\text{MCl}_2 \cdot 3\text{H}_2\text{O}$, and $\text{MCl}_2 \cdot 5\text{H}_2\text{O}$.

S11. The accompanying vapor pressure-composition diagram at 25°C is for water-XY systems, XY being a pure salt. (a) What is the lowest vapor pressure that could



be achieved when XY is used as a desiccant? (b) What would be the conditions for drying a wet sample of XY to give crystals of $XY \cdot 2H_2O$? (c) What is the mole % of water in a solution saturated with XY ? (d) What hydrates does the salt XY form?

S12. Besides low P_{H_2O} and high capacity, discuss other desirable properties of a practical desiccant.

S13. Name some mixtures over which $BaCl_2 \cdot 2H_2O$ may be prepared in a hydrostat at $25^\circ C$.

S14. Explain how to obtain $BaCl_2 \cdot H_2O$, starting with a wet sample of the crystalline dihydrate.

S15. Is $CaCl_2$ a good desiccant over which to cool ignited CaO ? Describe how CaO should be cooled after ignition.

S16. Devise an experiment to prove that $BaCl_2 \cdot H_2O$ exists, and to establish the conditions under which it is stable.

S17. Water- H_2SO_4 systems may be made up to give many of the water-vapor pressures of Table S10.1 (p. 683). Explain why a water- H_2SO_4 system giving a particular P_{H_2O} would generally not be as desirable as one of the systems in Table S10.1, as far as use in a hydrostat is concerned. (Find P_{H_2O} as a function of composition for water- H_2SO_4 systems, and consider its constancy as small amounts of water are absorbed.)

S18. Design simple equipment for the rapid equilibration of small (1–10 g) samples at room temperature, from any desired P_{H_2O} up to the saturation P_{H_2O} .

S19. Is it semantically proper to say that samples are “dried” in a desiccator? Give a more precise statement, and explain.

S20. Explain how you would bring an air stream flowing at 1.0 l/min (STP) to a water-vapor pressure of 10.0 mm at $25^\circ C$.

Section 10C

S1. How may $CaCO_3$ be maintained without decomposition at $800^\circ C$?

S2. What would be the minimum temperature required for decomposition of CaCO_3 in contact with a gas stream having a P_{CO_2} of 25 mm?

S3. Why does CaCO_3 not decompose very rapidly in a covered crucible at 650°C ? How could the decomposition be hastened at this temperature?

S4. In each case, explain why CaCO_3 may or may not be determined by measuring the loss in weight on ignition to 950°C , when the CaCO_3 is present in a two-component mixture with each of the following substances: NaCl , CaO , $\text{Ca}(\text{OH})_2$, CaSO_4 , $\text{Pb}(\text{NO}_3)_2$, ZnSO_4 , NaNO_3 , HgO , PbCl_2 .

S5. A precipitate is considered to be a suitable weighing form for gravimetric analysis with the thermobalance if the precipitate shows a temperature range over which its weight is constant. Explain.

S6. Devise and sketch a mechanical design for a thermobalance that will permit simultaneous heating and weighing of a small crucible. Modify a conventional type of balance. Do not include temperature controls, automatic weighing, etc. Check your design against those in the literature.

SUPPLEMENTARY PROBLEMS

Sections 10A, B

S1. With the data from Fig. S10.1 (p. 677), plot $\log P_{\text{H}_2\text{O}}$ against $1/T$, and determine the slope and intercept. Calculate the heat of dissociation and compare with the experimental value of 24.9 kcal/mole.

S2. With data from Fig. S10.1, find the constants for the $\log P_{\text{H}_2\text{O}}$ vs. $1/T$ equation. Use this equation to calculate: (a) $P_{\text{H}_2\text{O}}$ at the experimentally inconvenient temperatures of 280 and 830°C ; (b) temperatures at which $P_{\text{H}_2\text{O}}$ equals 1.4 mm and 3 atm.

S3. A 1.000-g sample of CaO is put in a tube maintained at 800°C . A nitrogen stream is passed through the tube at the rate of 0.50 l/min (measured at 800°C and 760 mm). Explain carefully what happens if, at 10-minute intervals, the water content of the nitrogen stream is increased in steps of 100 mm. (State any reasonable assumptions made in presenting the answer.)

<i>Ans.</i>	Time interval (min).....	0-10	10-20	20-30	30-32.4	32.4-40
	Influent $P_{\text{H}_2\text{O}}$, mm.....	100	200	300	400	400
	mmoles H_2O absorbed by CaO ...	0	.0030	.0105	.0043	0
	Effluent $P_{\text{H}_2\text{O}}$, mm.....	100	160	160	160	400

S4. What is the weight percentage of each component in an aqueous solution containing 50.0 mole % of H_2SO_4 ?

S5. Compute the mole percentage of each component in the following mixtures: (a) 70.0 g NaCl and 50.0 g H_2O ; (b) 10.0 g BaCl_2 , 40.0 ml H_2O , and 5.0 g KNO_3 ; (c) 5.0 ml conc. H_2SO_4 and 6.0 ml conc. HNO_3 (Appendix IVB, p. 913); (d) air, containing by volume 21.0% O_2 , 78.0% N_2 , and 0.03% CO_2 . (Why do these not total to 100.0%?) *Ans.* (b) 2.07 mole % BaCl_2 , 95.8 mole % H_2O , 2.14 mole % KNO_3 .

S6. Using Fig. S10.2 (p. 679), find the equilibrium $P_{\text{H}_2\text{O}}$ at 25°C of a system containing (a) 2.05 moles BaCl_2 and 3.00 moles H_2O , (b) 2.97 moles BaCl_2 and 7.30 moles H_2O , (c) 1.00 mole BaCl_2 and 108.3 moles H_2O , (d) 200.0 g BaCl_2 and 10.0 g H_2O , (e) a BaCl_2 -water mixture containing 28.0% water by weight, (f) a 1.2 M BaCl_2 solution. *Ans.* (d) 0.2 mm.

S7. A BaCl_2 -water system contains 75.0% by weight of BaCl_2 . (a) Give the mole percentages of BaCl_2 and water. (b) What are the stable phases present? (c) Give the weight percentages of each stable phase. *Ans.* (a) 20.60 mole % BaCl_2 ,

79.4 mole % water; (b) dihydrate and saturated solution;

(c) 82.4 wt. % dihydrate, 17.6 wt. % saturated solution.

S8. A BaCl_2 -water system contains 75.0 mole % BaCl_2 . What are the stable solid phases present? Give the weight percentages of each.

S9. Within what range of relative humidity at 25°C may $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ be prepared by the air-drying of a wet sample? *Ans.* 24–90%.

S10. Following are vapor pressures at 25°C for Na_2CO_3 -water systems: water, 23.8 mm; sat. Na_2CO_3 (30.3 g Na_2CO_3 per 100 g water), 21.2 mm; $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ - $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ mixture, 17.7 mm; $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ - Na_2CO_3 mixture, 4.7 mm. A desiccator contains 1 mole anhydrous Na_2CO_3 . Draw an approximate plot of $P_{\text{H}_2\text{O}}$ as a function of water added to the desiccator, up to 200 g of added water.

S11. Draw a P - C diagram and describe the hydrates that are probably formed, using the following data for CuSO_4 -water systems at 25°C . In each pair of numbers, the first is the $P_{\text{H}_2\text{O}}$ in millimeters of a system whose mole % of water is given by the second number: 0.1–0, 0.8–20, 0.9–40, 2.0–50, 5.6–60, 5.8–70, 7.0–75, 7.8–80, 7.9–82.5, 23.0–85, 23.0–90, 22.9–95, 23.0–97.4 (sat. soln.), 24.0–100.

Ans. Mono-, tri-, and pentahydrate.

S12. From the data of Fig. S10.3 (p. 681), draw an approximate P - C diagram for the BaCl_2 -water system at 45°C .

S13. In Table S10.1 (p. 683), water in the effluent gas stream is expressed in millimeters. (a) How many milligrams of water are there per liter of an air mixture at 30°C whose $P_{\text{H}_2\text{O}}$ is 1.00 mm? (b) What is the conversion factor for converting millimeters to milligrams per liter at 30°C ? (c) At what temperature would the conversion factor be 1.00? *Ans.* (a) 0.95 mm; (b) 0.95; (c) 16°C .

S14. From the data in Table S10.1, draw approximate P - C diagrams at 25°C for the systems: (a) K_2CO_3 -water, (b) Na_2SO_4 -water, (c) Na_2HPO_4 -water. Why might these diagrams be incomplete?

S15. A system containing 104.1 g BaCl_2 and 23.4 g water is put into a box of 2000 l of dry air at 25°C and 760 mm. What $P_{\text{H}_2\text{O}}$ is established? How much water goes into the gas phase, and what is the composition of the final BaCl_2 -water system?

Ans. 5.7 mm, 0.61 mole H_2O , 0.31 mole monohydrate and 0.19 mole dihydrate.

S16. Suppose that the 2000 l of dry air in Prob. S15 are slowly and continuously swept through the BaCl_2 -water mixture, so that the effluent stream contains the equilibrium $P_{\text{H}_2\text{O}}$ of the water-salt mixture at all times. How much water would go into the gas phase, and what would be the final composition of the BaCl_2 -water system? Compare answers with Prob. S15, and discuss.

Ans. 0.80 mole, 0.50 mole monohydrate and 0.001 mole anhydrous BaCl_2 .

S17. Rework Probs. S15 and S16 for the case where only 200 l of air are used.

S18. Find vapor pressure-composition data for Na_2HPO_4 -water systems, and construct P - C and P - T diagrams similar to Figs. S10.2 and S10.3 (u7).

S19. From the data of Fig. S10.3, prepare a $\log P$ vs. $1/T$ curve for the decomposition of $\text{BaCl}_2 \cdot \text{H}_2\text{O}$. At what temperature is the decomposition pressure equal to 1 atm? Is the temperature specified in Exp. 10.1 adequate for drying BaCl_2 ?

Ans. 142°C ; yes.

S20. Two equations that have been much used to represent Type I isotherms are the Freundlich and Langmuir equations (M25).

$$M = aP^b \quad (\text{Freundlich})$$

$$M = \frac{qkP}{1 + kP} \quad (\text{Langmuir})$$

M is the mass of adsorbate per unit mass of adsorbent, and P is the equilibrium vapor

pressure of the adsorbate. The remaining parameters (a , b , q , and k) are constants characteristic of the particular adsorbent-adsorbate system: they are temperature dependent.

(a) Explain how a plot of $\log M$ vs. $\log P$ permits evaluation of a and b in the Freundlich equation.

(b) Explain how a plot of P/M vs. P permits evaluation of k and q in the Langmuir equation.

(c) Find the limiting value of the slope dM/dP (as P approaches zero) for each equation, and explain why the Langmuir equation gives a more reasonable value.

(d) Find the limiting value of M as P becomes very large, and explain why the Langmuir equation gives a more reasonable value.

S21. Consider qualitatively the nature of the forces acting on a molecule of a liquid in a concave surface layer having a very high radius of curvature, as at the top of a column of liquid that stands in a very fine capillary pore, and explain why easier condensation of the liquid might be expected at this surface than at a large plane surface.

It may be shown from thermodynamic principles that

$$\log \frac{P}{P_0} = - \frac{2M\gamma}{2.303RT\rho r}$$

P_0 is the vapor pressure of the pure liquid, measured from a large plane surface, as it stands in a beaker. P is the vapor pressure of the liquid from a concave surface having a radius of curvature, r (in centimeters). M and ρ (in g/cc) are the molecular weight and density of the liquid. R is the gas constant (1.9872 cal deg⁻¹ mole⁻¹, or 8.3144×10^7 ergs deg⁻¹ mole⁻¹), and T is the absolute temperature (°K). The surface tension is γ (in dynes/cm) (M25).

Find the values of these properties for water at 25°C, and calculate the ratio P/P_0 , assuming that r for a typical capillary pore in an adsorbent is 15Å. Explain how your answer ($P/P_0 = 0.5$) supports the above statement that a liquid will condense more easily at the surface of a capillary than at a large plane surface.

S22. A 30.0-g sample of absolute ethanol requires 20.7 ml of Karl Fischer reagent for titration. The water titer of this reagent is 2.50 mg/ml, which means that one milliliter of the reagent is equivalent to 2.50 mg of water. What is the % water in the sample?

S23. Suppose that a Karl Fischer titration of 50 ml of solution is carried out in a 250-ml flask at 25°C, and that the space above the solution in the flask is inadvertently filled with undried air from the room ($P_{H_2O} = 20$ mm). How much of the reagent in Prob. S22 would be used to titrate this water? (In practice, of course, the solution contacts more air than this, and removes even more water, unless special precautions are employed to keep the system dry.) Ans. 1.5 ml.

S24. If the standard iodine solution used in a Karl Fischer titration contains 20.0 mg of iodine per ml, how much water would 1.00 ml of this reagent react with?

Section 10C

S1. From the data of Fig. S10.5 (p. 691), calculate the heat of dissociation of $CaCO_3$, and evaluate the constants in an equation of the type

$$\log P_{CO_2} = A/T + B$$

(a) Calculate P_{CO_2} at 550°C and at 937°C, and compare with the experimental values of 0.4 and 1346 mm, respectively.

(b) Calculate the temperature at which P_{CO_2} is 0.80 mm.

S2. A gas mixture containing 0.188 g/l CO_2 , 0.1457 g/l O_2 , and 0.0420 g/l N_2 is passed over CaO at 760 mm and 800°C . (a) What are the partial pressures of CO_2 , O_2 , and N_2 in the entering stream? (b) Does any change in weight of the CaO occur? If so, what is the P_{CO_2} in the effluent stream, as long as any CaO remains in the sample? (c) What changes would occur if the P_{CO_2} in the influent stream were 140 mm?

S3. Air contains 0.030% CO_2 by volume. (a) Calculate P_{CO_2} in atmospheres and in millimeters. (b) At what temperature does CaCO_3 decompose in air? (Use the equation derived in Prob. S1.) (c) For gravimetric analysis, Ca is often precipitated as CaC_2O_4 , which may be decomposed to CaCO_3 at an appreciable rate by being heated above 500°C in air. Specify the temperature range for the formation of CaCO_3 in air. How might this range be increased?

Ans. (a) 0.00030 atm, 0.23 mm; (b) 530°C ; (c) $500\text{--}530^\circ\text{C}$.

S4. Data are given below for the thermal decomposition of NaHCO_3 , for temperatures at which Na_2CO_3 is perfectly stable (U7). (a) Calculate the equilibrium constant for the reaction at 100°C . (b) It is desired to dry NaHCO_3 by heating at 100°C in an air stream with a $P_{\text{H}_2\text{O}}$ of 15 mm. What would P_{CO_2} have to be in order to prevent decomposition of the NaHCO_3 ? Is this practical? (c) Devise a method for drying NaHCO_3 without decomposition. (d) Outline a method for analyzing a mixture of NaHCO_3 , Na_2CO_3 , and small amounts of water by a loss-in-weight procedure.



Temperature ($^\circ\text{C}$) . . .	70	80	90	100	110
Total pressure (atm) . .	.158	.301	.545	.962	1.648

S5. If 0.500 g of pure Ag_2O is heated in a closed 200-ml flask at 125°C , what percentage of the Ag_2O is decomposed according to the following reaction? (At 125°C the equilibrium pressure is 110 mm.)



Ans. 82%.

S6. The P - T curve for the decomposition of Ag_2O (see Prob. S5) is given by $\log P = -2859/T + 6.285$. P is in atmospheres, and T is the absolute temperature. At what temperature does Ag_2O decompose (a) in pure oxygen at 760 mm, and (b) in air at 760 mm?

S7. In the pyrolysis curve for $\text{Cu}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in Fig. S10.6 (p. 693), what are the relative heights of the steps?

Ans. 295.63 : 142.55 : 79.54.

S8. A 1.0500-g sample contains excess water, inert material, and the nitrates of Ag and Cu . At various temperatures in the thermobalance, the sample shows the following constant weights: 0.9053 g at 50° , 0.7522 g at 175° , 0.6892 g at 380° , 0.5032 g at 800° . Calculate the composition of the mixture.

S9. The pyrolysis curve for CaC_2O_4 obtained with the thermobalance shows the following constant-weight regions: $18\text{--}120^\circ$ ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$), $226\text{--}398^\circ$ (CaC_2O_4), $478\text{--}660^\circ$ (CaCO_3), $890\text{--}1000^\circ$ (CaO). For MgC_2O_4 , the regions are: $18\text{--}176^\circ$ ($\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$), $223\text{--}397^\circ$ (MgC_2O_4), $480\text{--}1000^\circ$ (MgO). (a) Sketch each curve, showing approximately the correct relative heights for the steps in each curve. (b) A 0.6000-g sample contains excess water, inert material, CaC_2O_4 , and MgC_2O_4 . At various temperatures in the thermobalance, the sample shows the following constant weights: 0.5406 g at 100° , 0.4685 g at 300° , 0.3477 g at 500° , 0.2194 g at 900° . Calculate the composition of the mixture.

Ans. 70.00% $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$,
13.45% $\text{MgC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, 9.89% H_2O , 5.67% inert.

SOLUBILITY AND SOLUBILITY PRODUCT

ACTIVITY PRODUCTS

(See Sec. 11D, p. 171)

Activity Coefficients

Instead of a K_s expression employing molar concentrations, activities may be employed. An equilibrium constant using molar concentrations is called a *concentration equilibrium constant*, whereas one using activities is called an *activity equilibrium constant*, or a *thermodynamic equilibrium constant*. Activity constants are symbolized by the superscript $^\circ$. Thus for BaSO_4 ,

$$K_s = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \quad (\text{Concentration constant}) \quad (Sa)$$

$$K_s^\circ = [a_{\text{Ba}^{2+}}][a_{\text{SO}_4^{2-}}] \quad (\text{Activity constant}) \quad (Sb)$$

K_s° is strictly constant and independent of inert electrolytes. Unless designated otherwise, the values in Appendix V are really activity solubility products.

The activity (a_i) of an ion species, i , is related to its molar concentration $[i]$ by means of the activity coefficient, γ_i .

$$a_i = \gamma_i[i] \quad (Sc)$$

From Eqs. *Sb* and *Sc*, the activity solubility product in terms of molar concentrations and activity coefficients is

$$K_s^\circ = (\gamma_{\text{Ba}^{2+}})[\text{Ba}^{2+}](\gamma_{\text{SO}_4^{2-}})[\text{SO}_4^{2-}] \quad (Sd)$$

From Eqs. *Sa* and *Sd*,

$$K_s = \frac{K_s^\circ}{(\gamma_{\text{Ba}^{2+}})(\gamma_{\text{SO}_4^{2-}})} \quad (Se)$$

In similar manner, for the generalized solute A_nB_m :

$$K_s^\circ = (\gamma_{\text{A}})^n[\text{A}]^n(\gamma_{\text{B}})^m[\text{B}]^m \quad (Sf)$$

$$K_s = \frac{K_s^\circ}{(\gamma_{\text{A}})^n(\gamma_{\text{B}})^m} \quad (Sg)$$

Accepting the fact that K_s values increase with electrolyte concentration (Fig. 11.4, p. 172), and that K_s° values are defined as constant, it is apparent from Eqs. *Se* and *Sg* that activity coefficients decrease with increase in electrolyte concentration. This effect is greater for ions of higher charge. It may be shown (**D1**) on theoretical grounds that

$$\log \gamma_i = \frac{-0.5085 z_i^2 \sqrt{\mu}}{1 + 0.3281 \alpha_i \sqrt{\mu}} \quad (\text{At } 25^\circ\text{C}) \quad (Sh)$$

where γ_i is the activity coefficient of the ion species, i ,

z_i is the charge on the ion species, i ,

α_i is the effective diameter in Å of the (hydrated) ion species, i ,

μ is the ionic strength of the solution, defined as $\frac{1}{2} \sum [i] z_i^2$, for all ion species in solution.

The constants 0.5085 and 0.3281 are temperature dependent and are known for other temperatures (**B5**).

The decrease of activity coefficients with increase in inert-electrolyte concentration may be regarded as a decrease in effective concentration of the ions. For a part of the time, an ion of the insoluble substance is surrounded by enough oppositely charged ions so that its behavior is restricted as if it were in a neutral molecule.

Activity coefficients may be calculated from Eq. *Sh*. Values of μ and z_i are obtained from the ion concentrations and charges in the system under consideration. Values of α_i are known empirically for many common ions, and are tabulated in Appendix VI (p. 921). However, to avoid time-consuming computations, Appendix VI also lists values of γ_i as calculated for different values of μ , α_i , and z_i . With such estimates of activity coefficients, solubility-product calculations may be performed somewhat more accurately than by the elementary procedure. Illustrative examples of such calculations are given below.

Example S1. Calculate the ionic strength in a solution containing 0.020 *M* $(\text{NH}_4)_2\text{SO}_4$, 0.050 *M* NH_4Cl , and 0.030 *M* $\text{Al}_2(\text{SO}_4)_3$.

$$\mu = \frac{1}{2}[(0.090 \times 1^2) + (0.110 \times 2^2) + (0.050 \times 1^2) + (0.060 \times 3^2)] = 0.56$$

$\begin{array}{cccc} \uparrow & \uparrow & \uparrow & \uparrow \\ \text{—NH}_4^+ & \text{—SO}_4^{2-} & \text{—Cl}^- & \text{—Al}^{3+} \end{array}$

It should be noted that: (1) Only strong electrolytes contribute to the ionic strength. Weak electrolytes, such as acetic acid, do not contribute appreciably. (2) Any electrolyte whose concentration is low compared to that of other electrolytes present may be considered to contribute only negligibly to the ionic strength.

Example S2. Estimate the activity coefficient of sulfate in 0.033 *M* Na_2CO_3 .

$$\mu = \frac{1}{2}[2 \times 0.033 \times 1^2 + 0.033 \times 2^2] = 0.099, \text{ or about } 0.10$$

From Appendix VI, for divalent SO_4^{2-} , α is 4 Å, and γ is 0.355 at an ionic strength of 0.10.

Example S3. K_s° for BaSO_4 is 1.00×10^{-10} (Appendix V). Compute the solubility of BaSO_4 in $0.015\text{ }M$ KCl (a) with no consideration for activity effects, and (b) using activity coefficients. (c) Compare answers with the experimental value obtained from Fig. 11.3 (p. 171).

$$(a) \quad [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.00 \times 10^{-10}$$

Letting the molar solubility of BaSO_4 be x , we obtain

$$[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = x$$

Therefore

$$(x)(x) = 1.00 \times 10^{-10}$$

$$x = 1.00 \times 10^{-5}\text{ }M, \text{ or } 2.33\text{ mg/l of BaSO}_4$$

$$(b) \quad (\gamma_{\text{Ba}^{2+}})[\text{Ba}^{2+}](\gamma_{\text{SO}_4^{2-}})[\text{SO}_4^{2-}] = 1.00 \times 10^{-10}$$

Estimate activity coefficients:

$$\mu = \frac{1}{2}[0.015 \times 1^2 + 0.015 \times 1^2] = 0.015$$

(It is assumed that the small concentration of BaSO_4 does not significantly contribute to μ . This assumption may be checked and found valid after the answer is obtained.)

$$\text{From Appendix VI for an ionic strength of } 0.015, \quad \gamma_{\text{Ba}^{2+}} = 0.63, \gamma_{\text{SO}_4^{2-}} = 0.62$$

Letting the molar solubility of BaSO_4 be y , we obtain

$$[\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = y$$

Therefore

$$(0.63y)(0.62y) = 1.00 \times 10^{-10}$$

$$y = 1.60 \times 10^{-5}\text{ }M, \text{ or } 3.74\text{ mg/l}$$

(c) The value y agrees considerably better than x with the experimental value of 4.3 mg/l , taken from Fig. 11.3. Discrepancies are larger for ions of higher charge.

It should be pointed out that Eq. *Sh* assigns all activity effects to the charge and radius of the ions, and is therefore only an approximation. The activity of a solute species depends upon the specific chemical forces between ions, as well as on electrostatic forces. Equation *Sh* is a *limiting law*, which becomes more accurate as μ approaches zero. (Note that γ approaches unity as μ approaches zero.)

Experimental Determination of K_s° Values

To determine a K_s° value accurately, the empirical and approximate activity coefficients of Appendix VI may be circumvented by the following procedure: (1) K_s values are determined for the insoluble substance at different ionic strengths, that is, in solutions containing various concentrations of an inert electrolyte. (2) These K_s values are then plotted against $\sqrt{\mu}$.* This plot is extrapolated to zero ionic strength.

*The square root of μ is used because this plot approaches a straight line at low ionic strengths, and can be extrapolated more easily to zero ionic strength than the nonlinear plots of other functions of μ .

The value of K_s at $\mu = 0$ is K_s° . As μ approaches zero, the activity coefficients approach unity, and K_s approaches K_s° , according to Eq. Sg.

Activity Coefficients in Other Types of Equilibria

The principles discussed in the previous sections apply to other kinds of equilibrium constants, such as acid-base ionization constants, redox equilibrium constants, and complex formation or dissociation constants. Examples of calculations are given later in the text, along with the discussions of each of these kinds of equilibrium constants.

ACCURACY OF SOLUBILITY-PRODUCT CALCULATIONS

As mentioned on page 161, the solubility (and therefore K_s) of an ionic precipitate is dependent upon many factors. Not all of these may be known and defined in the particular system for which a solubility-product calculation is being made, in which case the calculation may be in error. Further, the experimental conditions under which the solubility-product values in Appendix V were measured were not all well defined, and many of the values are inaccurate.

Any computation involving solubility products should be regarded as an approximation that may be several-fold in error. The factors that may cause error in the measurement or use of solubility-product values are classified below, and are very ably discussed in greater detail by Leussing (L7) and Lewin (L8).

Factors That May Cause Error in Solubility-Product Calculations

Nature of the solid

Polymorphism. Polymorphic forms of a substance are identical in composition, but differ in physical properties, such as density, color, crystal structure, etc. Inspection of Appendix V reveals several substances (especially hydroxides and sulfides) that can exist in polymorphic forms, each with a different solubility product.

Except at the transition temperature, only one polymorph is stable under a given set of conditions, and the other forms gradually change into this stable form. However, the rate of transition may be low, and metastable forms may exist for long times before reversion to the stable form. The metastable forms have higher energy contents and higher solubilities than the stable form, and the difference may be considerable. Thus, K_s values for metastable forms may range from slightly larger to thousands of times larger than the K_s value for the stable form.

Polymorphism is probably the major cause of discrepancies in K_s values reported in the literature. It cannot be tacitly assumed that the

form at hand is the stable form. In fact, rapid precipitations of the type performed in analytical processes usually yield metastable states that slowly transit to the stable state. The transition may take minutes, hours, days, weeks, or even years in some cases. This is one reason why a freshly formed precipitate often has a markedly higher solubility than the aged form.

In the case that polymorphic forms of a substance exist, no single value of K_s can characterize the substance. Each form has its own solubility and its own K_s , which can be measured only if each form can be brought into equilibrium with its own saturated solution. On the other hand, if a preparation contains more than one form, then a "saturated" solution of the preparation is not at equilibrium, and any "solubility" or "solubility product" measured on such a preparation has no meaning. Many solubility products reported in the literature have undoubtedly been measured on systems of this sort.

Hydration. If a substance can exist in two different hydrated forms, each has a different energy content, a different solubility, and a different solubility product (except at the transition temperature). What has been written in the preceding section about polymorphs applies largely to hydrates also, with perhaps one modification: transition times for hydrates are fairly short, and metastable hydrates are not usually very long-lived in aqueous systems. For this reason, K_s values for differently hydrated forms of a particular substance are rarely found in the literature; instead, only the solubility product of the stable form is given.

Particle size. The solubility of a small particle of a given substance is greater than the solubility of a large particle. This phenomenon may be explained by considering the nature of the forces on a surface molecule.

A molecule which lies in a sharply convex surface is less completely surrounded by its neighbors than one which lies in a flat surface, as depicted in Fig. S11.1. The attractive forces exerted upon a molecule in a sharply convex surface by its neighbors will therefore be less, and the surface molecules will therefore be more easily able to leave the surface and go into solution.

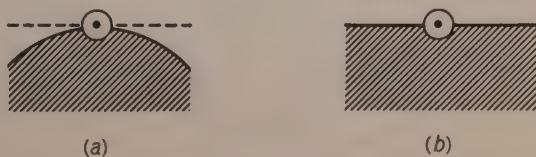


FIG. S11.1. Forces on Surface Molecules—A surface molecule, represented by a dot within a circle, is less completely surrounded by its neighbors when the surface is convex (a) than when the surface is plane (b). (Reprinted in part from K. J. Mysels, *Introduction to Colloid Chemistry* [New York: Wiley, 1959], Fig. 8-9, by permission of the publisher.)

Based on such considerations, a theoretical expression** may be derived for the solubility of small, spherical particles as a function of particle size (B28, V1).

$$\log \left(\frac{S_r}{S} \right) = \frac{2M\gamma}{2.303iRT\rho r}$$

S_r is the solubility of a particle of radius, r . S is the equilibrium solubility of massive particles. M is the molecular weight of the solute. R is the gas constant, 8.314×10^7 (dyne-cm)(mole) $^{-1}$ (deg) $^{-1}$. T is the absolute temperature. The interfacial tension between solvent and solute is γ , in dynes per centimeter. The density of the solid is ρ , in grams per cubic centimeter. The factor i is the van't Hoff coefficient, and represents the average number of ions given per molecule of solute. For nonspherical particles, the form of the equation above is the same, but the right side must be multiplied by shape factors that do not differ greatly from unity.

Table S11.1 gives data for calculating S_r/S for various substances. It may be seen that fine crystals of some substances theoretically have appreciably higher solubilities than coarse crystals.

TABLE S11.1

DEPENDENCE OF SOLUBILITY UPON PARTICLE SIZE FOR VARIOUS SUBSTANCES
AT 25°C*

Substance	Molecular Weight	Density, ρ (g/cc)	Diameter, $2r$ (microns)	Surface Tension, γ (dynes/cm)	Hardness (Mohs' scale)	S_r/S	i
PbI ₂	461	6.16	0.4	130	Very soft	1.02	2.0
CaSO ₄ ·2H ₂ O.....	172	2.32	0.2-0.5	370	1.6-2	1.04-1.12	1.6
Ag ₂ CrO ₄	332	5.52	0.3	575	~2	1.10	2.0
PbF ₂	245	8.24	0.3	900	~2	1.09	1.7
SrSO ₄	184	3.96	0.25	1400	3.0-3.5	1.26	1.8
BaSO ₄ (Hulett).....	233	4.5	0.1	1250	2.5-3.5	1.80	2.0
(Dundon).....	233	4.5	0.2	3000	2.5-3.5	1.90	2.0
CaF ₂	78	3.18	0.3	2500	~4	1.18	2.0

*Data taken from M. L. Dundon, *Journal of the American Chemical Society*, 45, 2658 (1923), Table 2, with permission of the copyright owner, the American Chemical Society.

If a precipitate consists of very small particles, then a solution that is saturated with respect to them is supersaturated with respect to bulk-sized particles, and the solubility-product principle does not apply in such a nonequilibrium system. The increase in solubility with decrease

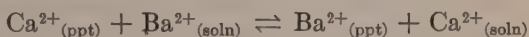
**Note the similarity between this expression and that in Prob. S21 (p. 699). The same considerations explain why the vapor pressure of a very small droplet of a liquid is greater than that of the bulk liquid, and also why the vapor pressure of a liquid in a capillary is greater than that of the bulk liquid.

in particle size is another reason why the solubility product of a freshly formed precipitate is sometimes larger than the solubility product for an aged precipitate.

While the preceding equation for S_r/S is probably valid, it is not permissible to extend it to very small particle sizes, for it predicts that the solubility should become very great as the size becomes very small. This is not the case experimentally, for solubilities many times in excess of the equilibrium solubility have never been established. Also, the very existence of colloidal particles indicates that other factors besides size influence the solubility. By considering that the particles are charged, Knapp shows theoretically that although the equation above approximates the behavior of large particles, S_r/S reaches a maximum and then decreases with decreasing particle size after a critical size is reached (K9).

Impurities in the precipitate. When thrown down from a solution containing impurities, some precipitates consist of mixed crystals or solid solutions, and may be entirely different in nature from the pure precipitates. "Solubility-product" values measured in such mixtures may not be taken as identical to the values for the pure substances. Before accepting a value for a solubility product, it must be ascertained that the solid phase in question is pure. Thus, AgBr is much more insoluble than AgCl, and it might be supposed that AgBr carefully precipitated in the presence of chloride would not contain chloride. However, such AgBr may contain significant amounts of AgCl, and its solubility may be quite different from that of pure AgBr.

The amounts of an impurity need not always be large to affect the solubility of a precipitate. An ionic impurity capable of exchanging with a precipitate may have a great influence upon its "solubility." Thus, when pure CaC_2O_4 is put into a solution containing small amounts of Ba^{2+} , the Ba^{2+} ions exchange with Ca^{2+} ions in the precipitate, liberating the Ca^{2+} into solution.



(This type of process is called *surface-exchange adsorption*, and may occur appreciably even though BaC_2O_4 is much more soluble than CaC_2O_4 .) The net effect of the exchange is to create a nonequivalence between the Ca^{2+} and the $\text{C}_2\text{O}_4^{=}$ in solution, the $[\text{Ca}^{2+}]$ lying above, and the $[\text{C}_2\text{O}_4^{=}]$ lying below the value given by a saturated solution of pure CaC_2O_4 in pure water. Other ions showing a similar effect are $\text{SO}_4^{=}$, IO_3^- , and OH^- .

The effect of surface-exchange adsorption upon solubility may be small. The effect is a function of the amount of surface that is available for exchange. It is significant only for finely divided precipitates, and

becomes larger as the amount of precipitate per unit volume of solution increases.

Surface-exchange adsorption may occur not only with impurities present in the solution in which the precipitate is dissolved, but even precipitates that have been formed and purified in another medium may carry such exchangeable impurities by coprecipitation.

Inert-electrolyte effect. If activity coefficients are neglected, only rough approximations may be made of the solubility of a slightly soluble substance in solutions containing other electrolytes. Up to concentrations of a few hundredths molar, the calculated solubility may differ several times from the observed one. In more concentrated solutions, discrepancies of the order of tenfold or even higher may occur, especially for substances with ions of higher charge, such as BaSO_4 .

Estimated activity coefficients (p. 702) give better approximations. Up to ionic strengths of 0.1, estimated solubilities usually differ from experimental ones by a factor of less than 2, even for salts with ions of higher charge. It must be emphasized that the use of activity coefficients is semi-empirical and gives only estimations. The methods described previously do not apply to ionic strengths above 0.1. Equation *Sh* (p. 702) does not hold at higher ionic strengths, since activity coefficients become dependent upon the specific chemical properties of the ions instead of upon just the charge and radius.

In the sense that an inert electrolyte may increase the solubility of a slightly soluble salt several times, the effect may be considered rather large. However, compared to the common-ion effect, which may depress a solubility by a thousandfold or more, the inert-electrolyte effect is usually small. Most of the calculations of quantitative analysis involve common- or reactive-ion effects, and the inert-electrolyte effect may be neglected with comparatively little error.

Chemical reactions. The solubility-product principle, as defined and utilized in elementary fashion (Sec. 11B, p. 164), is of rather limited application. The principle applies only to slightly soluble, completely ionized substances, and the elementary problem-working procedure applies only when the behavior of the solute is describable by a single chemical equation. This elementary procedure does not apply to some salts, like HgCl_2 , an appreciable portion of which exists in forms other than Hg^{2+} and Cl^- in solution. The equilibria necessary to describe HgCl_2 are given on page 161, and to write only



implies a simplicity that is misleading, incomplete, and useless by itself. Such solutes must be described by several equilibrium constants, the methods of Chapter 17 being used. There is good evidence that some

metallic hydroxides and sulfides exist partially in undissociated form in solution.

Even substances that do not themselves ionize in complicated fashion may react with water or other substances present in such a way that several equilibria must be used to describe their behavior. Some solutes behave in so complicated a way that it is questionable if the equilibria will ever become quantitatively known, except roughly. Among these are some oxalates, halides, hydroxides, and sulfides. Although K_s values are given for these substances in Appendix V, these values should be used with reservations. Examples are given below of reactions that may cause gross errors in solubility-product calculations if unrecognized. (A knowledge of hydrolytic and complex equilibria is prerequisite for quantitative treatment of these examples.)

Hydrolysis, or acid ionization of metal ions. Most metal ions have acid properties and hydrolyze. In weakly acid or basic solutions, the concentrations of the hydrolyzed forms may far exceed the concentrations of the unhydrolyzed aquated ions. Thus, in calculating the solubility of $\text{Al}(\text{OH})_3$ in water, it is insufficient to consider that the only important reaction is



In addition, it must be recognized that the Al^{3+} is a moderately strong acid, and that it exists principally in the form of species like AlOH^{2+} , $\text{Al}(\text{OH})_2^+$, and perhaps even some undissociated $\text{Al}(\text{OH})_3$. Accurate quantitative treatment of systems containing many solute species is difficult.

In Appendix V, the section on hydroxides contains values for the first acid ionization constants (i.e., hydrolysis constants) of most of the common metal ions. These values permit a rough decision on the relative importance of the acid ionization under a given set of conditions. The acid ionization may be very important in the case of species like Fe^{3+} , which hydrolyze strongly even in moderately acid solutions.

The anions of most insoluble salts have basic properties, and these may also hydrolyze when the salt is dissolved in water, as shown in the following illustrative example.

Example. Calculate the molar solubility of MnS from its solubility product: (a) neglecting the hydrolysis of S^- and (b) accounting for hydrolysis of S^- .

(a) If the molar solubility of MnS is x , then by the elementary method,

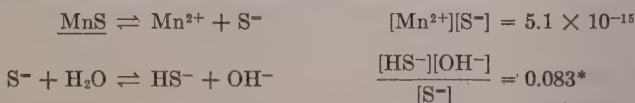
$$[\text{Mn}^{2+}][\text{S}^-] = K_s$$

$$(x)(x) = 5.1 \times 10^{-15}$$

$$x, \text{ or the molar solubility of } \text{MnS} = 7.1 \times 10^{-8} M$$

This method is not adequate. Inspection of the basic ionization constant of S^{2-} (0.083) shows that only a small fraction of the total sulfide can exist as S^{2-} in neutral or weakly basic solutions.

(b) The correct approach is to recognize that two equilibria are important, and that the S^{2-} from the MnS will ionize as a base:



The above two equations contain four (unknown) concentrations. Two more equations may be obtained from material balances:

$$\begin{array}{l} [HS^{-}] = [OH^{-}] \\ [Mn^{2+}] = [S^{2-}] + [HS^{-}] \end{array}$$

These four simultaneous equations may be solved to give

$$\begin{array}{l} [S^{2-}] = 6.8 \times 10^{-10} M \\ [HS^{-}] = [OH^{-}] = 7.5 \times 10^{-6} M \\ [Mn^{2+}] = 7.5 \times 10^{-6} M \end{array}$$

The molar solubility of MnS is therefore $7.5 \times 10^{-6} M$, about one hundredfold greater than the value calculated erroneously above.

All of the above-mentioned hydrolytic equilibria involve H_3O^{+} or OH^{-} . The solubility of a hydrolyzable salt is therefore pH -dependent. This is another way of explaining that the solubility of a hydrolyzable salt cannot be computed legitimately from the solubility product alone. As shown in the above example, it is useless to compute the solubility of a metal sulfide (such as MnS) from its solubility product alone. The ion S^{2-} combines tightly with H^{+} , forming the very weak acids HS^{-} and H_2S . Solubilities of MnS are therefore critically dependent upon acidity, and may be calculated only by considering both the solubility product of MnS and ionization constants of H_2S . Many other insoluble salts (carbonates, chromates, fluorides, phosphates, cyanides, etc.) behave likewise. The same considerations extend to reactions of the cations. Thus most metal ions hydrolyze increasingly with increase in pH . In considering the solubility of a metal salt such as $Cu(IO_3)_2$, account must be taken of the distribution of the metal ion (Cu^{2+}) among its hydrolyzed forms ($CuOH^{+}$, etc.). In fact, when the pH becomes sufficiently high, the metal salt, $Cu(IO_3)_2$, is no longer the most insoluble form; a basic salt, $CuOHIO_3$, or even the hydroxide, $Cu(OH)_2$, is formed instead.

In any particular problem, the relative importance of hydrolysis may be ascertained by: (1) noting if the pH of the solution differs significantly

*The magnitude of this equilibrium constant is given in Appendix VIIA.

from neutral, (2) noting if the solubility of the precipitate is *pH*-dependent, or (3) inspecting the magnitudes of the pertinent acid or basic ionization constants.

Complexation. Any complexing agent that reacts with either the cationic or anionic constituent of an insoluble salt will increase its solubility.

An example of cationic complexing is the well-known dissolution of $\text{Cu}(\text{OH})_2$ in ammoniacal solution, owing to formation of the $\text{Cu}(\text{NH}_3)_4^{2+}$ complex. Many other examples may be taken from organic substances that complex metal ions strongly, and that increase the solubilities of the metal salts. An example is EDTA (p. 574): the solubility of BaSO_4 in 1 *M* alkaline EDTA is about 0.1 *M*, as compared to 10^{-5} *M* in water.

An example of an increase in solubility due to anionic complexing is given in Table S11.2. The increased solubility of PbI_2 in $\text{Cd}(\text{NO}_3)_2$ over the solubility in a comparable concentration of $\text{Ca}(\text{NO}_3)_2$ is attributed to formation of stable and soluble $\text{Cd}^{2+}\text{-I}^-$ complexes ranging from CdI^+ to CdI_4^- .

TABLE S11.2
SOLUBILITY OF PbI_2 IN VARIOUS SOLUTIONS

Solution	Solubility of PbI_2
Water	0.0006 <i>M</i>
0.54 <i>M</i> $\text{Ca}(\text{NO}_3)_2$	0.0055 <i>M</i>
0.51 <i>M</i> $\text{Cd}(\text{NO}_3)_2$	0.038 <i>M</i>

According to the solubility-product expression, the solubility of a precipitate will diminish as excess precipitant is added to the solution (Fig. 11.2, p. 169). Sometimes, however, the precipitant forms higher soluble complexes, and the solubility trend will then reverse, the solubility of the precipitate increasing at higher concentrations of precipitant. An example is the redissolution of AgCl in an excess of NaCl (Fig. S13.1, p. 734). Other examples include metallic sulfides which dissolve in excess sulfide to form complex sulfanions (i.e., $\text{HgS}_2^{=}$), and amphoteric hydroxides (i.e., $\text{Zn}(\text{OH})_4^{=}$, $\text{Al}(\text{OH})_4^-$).

Accuracy of K_s Values

The sources of error described above operate in the determination of K_s values, as well as in solubility-product computations. Some of the K_s values reported in the literature are undoubtedly in error, having been determined without recognition of polymorphism, hydration, particle size, impurities, the inert-electrolyte effect, or other complicating equilibria.

Perusal of the literature shows that solubility products for some of the common precipitates have been determined many times and in many ways. For example, about fifty values are summarized by Bjerrum *et al.* (B13) for AgCl at various temperatures and ionic strengths.

Most of the values in Appendix V are taken from Bjerrum's work. Many represent medians of K_s° values (at 25°C) reported after 1950. Where recent values are not available, solubility products are listed in Appendix V from work published before 1950, or at different temperatures (indicated) or at different ionic strengths (indicated).

Where reported values for a particular substance range over several pK_s units, only the median is listed in Appendix V to the nearest pK_s unit. Where literature values range within a pK_s unit, the median is listed to the tenth of a pK_s unit. Solubility-product values given to the hundredth of a pK_s unit do not generally signify high accuracy, except for a few well-studied substances; in most cases, they represent single values, or medians of a few values.

The solubility products in Appendix V are adequate for problem working and exercises. However, before an unqualified value like those listed in Appendix V is used for accurate computations, the original literature should be consulted to find the conditions under which the value applies, and also to search for any error-causing factors that might have been operative during the determination of the value.

Spurious Accuracy in the Teaching of Solubility-Product Theory

At this point, the critical reader may have decided that the illustrative problems of this chapter are worked with spurious precision. This is correct. However, for the sake of clarity, it is probably best to teach solubility-product theory as if the K_s° values were precisely known. Values of K_s° *can* be precisely measured, and activity coefficients *can* be determined precisely for any system if desired. If the experimental methods used to determine most K_s° values *do* lack accuracy, or if we *do* introduce approximations in attempting to calculate activity coefficients, this should not detract from precise study of the theory. Therefore, in this text, problems involving solubility products (and other equilibrium constants) are worked with higher precision than may be warranted from the precision of the available experimental data.

SUPPLEMENTARY QUESTIONS

Section 11D

S1. Given the statement: $[\text{Ba}^{2+}][\text{SO}_4^{2-}] = K_s^\circ$. Under what conditions does this hold (a) precisely, (b) approximately, (c) poorly?

S2. Define the activity coefficient.

S3. Use Eq. *Sh* (p. 702) to describe the factors upon which the activity coefficient depends.

S4. Is it proper to think of the activity coefficient as a "chiseler's constant," or a "fudge factor," applied to make an inadequate generalization fit observed facts? (Consider that the activity coefficients, when found for a particular solute and a particular inert electrolyte, may be used to describe the behavior of many other systems of the same type.)

Section 11E

S1. Which form of $\text{Co}(\text{OH})_2$ in Appendix V is the stable form?

S2. At 20°C, anhydrite (CaSO_4) has a solubility of 2.87 g/l. The more stable gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) has a solubility of 2.31 g/l, or 2.04 g of CaSO_4 per liter. If one puts anhydrite into water with the intention of obtaining a saturated solution and of measuring K_s , explain what would probably happen. In view of your answer, speculate on how the figure of 2.87 g/l for the solubility of anhydrite may have been obtained, and interpret its meaning.

S3. Why should a large difference between solubility products of two different preparations of a particular substance (i.e., $\text{Ni}(\text{OH})_2$) be attributed to polymorphism rather than to a difference in particle sizes?

S4. One sometimes hears the statement: "When a very small value is obtained for an ion concentration as a result of a solubility-product calculation, it often bears no resemblance to the experimental value." Support this statement, and give it plausibility with a specific example.

S5. Suppose that there is given for $\text{Al}(\text{OH})_3$ just the solubility product $[\text{Al}^{3+}][\text{OH}^-]^3 = K_s$. According to this, how should the solubility of $\text{Al}(\text{OH})_3$ change with $[\text{OH}^-]$? Why is this conclusion invalid?

S6. Suppose that there is given for AgCl just the solubility product $[\text{Ag}^+][\text{Cl}^-] = K_s$. According to this, how should the solubility of AgCl depend upon $[\text{Cl}^-]$? Why is this conclusion invalid? (See p. 734.)

S7. In the illustrative example on page 710, explain carefully the basis of the two equations that were "obtained from material balances."

SUPPLEMENTARY PROBLEMS

Section 11B

S1. Express the relation between the molar solubility (s) and K_s for $\text{Pb}(\text{IO}_3)_2$ in " x " M $\text{Pb}(\text{NO}_3)_2$. When x is much greater than s , what sort of curve would be obtained if $\log x$ were plotted against $\log s$? *Ans.* $(s + x)(2s)^2 = K_s$; straight line.

S2. The insoluble salt AB is formed when the soluble strong electrolytes ACl and NaB are mixed. In terms of the solubility product of AB and the total concentrations of ACl and NaB in the mixed solution, formulate conditions obtaining when there is (a) no precipitation, (b) incipient precipitation (i.e., AB just begins to form), and (c) definite precipitation. Assume no supersaturation. Plot the relationship of $[\text{A}^+]$ to $[\text{B}^-]$ in the saturated solution, if K_s for AB is 1.0×10^{-10} . Indicate regions on this diagram where the foregoing three conditions exist.

S3. AgNO_3 solution is added slowly to a solution containing both Cl^- and I^- . At the point where the AgNO_3 added is just equivalent to the I^- , how high a concentration of Cl^- could exist in solution without precipitation of AgCl ? *Ans.* 0.0180 M .

S4. An excess of solid AgCl is placed in 1.00 l of 0.00100 M NaI . Give the concentrations of the various ion species in solution after equilibrium is attained, and also estimate how much solid AgCl disappears.

S5. Solid AgCl and AgBr are placed in contact with pure distilled water, so that both solubility products are satisfied. Give the equilibrium concentrations $[Ag^+]$, $[Cl^-]$, $[Br^-]$. Which salt makes the predominant contribution to $[Ag^+]$?

Ans. $[Ag^+]$, $[Cl^-] = 1.33 \times 10^{-6} M$;
 $[Br^-] = 3.7 \times 10^{-8} M$; AgCl.

Section 11D

S1. Compute the ionic strengths of (a) 0.010 M NaCl, (b) 0.025 M KNO_3 plus 0.019 M Na_2SO_4 , (c) m M KCl, or any 1-1 electrolyte, (d) m M Na_2SO_4 , or any 1-2 or 2-1 electrolyte, (e) m M $MgSO_4$, or any 2-2 electrolyte, (f) m M $Al_2(SO_4)_3$, or any 3-2 or 2-3 electrolyte. (Tabulate these results for use in later problems.)

Ans. (a) 0.010; (d) 3*m*.

S2. Estimate activity coefficients for Ag^+ and Cl^- in the following media: (a) 0.040 M KCl, (b) 0.025 M Na_2SO_4 plus 0.025 M $NaNO_3$.

S3. Calculate the solubility of $BaSO_4$ in 0.020 M $MgCl_2$ (a) neglecting activity effects, (b) using activity coefficients. Compare answers with Fig. 11.3 (p. 171).

Ans: (a) 2.33; (b) 5.3 mg/l.

S4. Calculate K_s for AgCl in 0.03 M $MgCl_2$, using the K_s° value given in Appendix V. Repeat for $BaSO_4$.

S5. What is the volume of 0.075 M HNO_3 required to dissolve 2.50 mg of $Co_2Fe(CN)_6$ computed (a) neglecting activity effects, (b) applying activity coefficients?

Ans. (a) 0.99; (b) 0.19 l.

S6. Rework some of the elementary text problems for Secs. 11B and 11C (pp. 174-76), correcting for activity effects. Compare answers with those originally obtained. Recommended problems are 10 and 11 of Sec. 11B and 5, 6, and 7 of Sec. 11C.

S7. Using Eq. *Sh* (p. 702), and values for α in Appendix VI, derive some of the activity coefficients in Appendix VI. (It is necessary to assign specific values to z_i and μ .)

S8. As the ionic strength approaches zero, show how $\log \gamma_i$ depends on ionic strength according to Eq. *Sh*. Using data from Appendix VI, draw plots of the activity coefficients of HSO_3^- , SO_4^{2-} , and PO_4^{3-} versus $\sqrt{\mu}$, and ascertain that they fit the theoretical dependence.

Ans. $\log \gamma_i = -0.5085 z_i^2 \sqrt{\mu}$.

S9. Using the Debye-Huckel law (Eq. *Sh*), ion diameters from Appendix VI, and solubility products from Appendix V, find the molar solubilities of the following salts in a KNO_3 solution as a function of ionic strength: AgCl, Ag_2CrO_4 , $BaSO_4$, $Mg_3(AsO_4)_2$. Insofar as is convenient, plot those solubility curves on a single plot, to bring out the effect of ionic charge. (Assume that there are no other complicating equilibria.)

Section 11E

S1. Calculate $[Hg^{2+}]$ in a pure water solution saturated with HgS, assuming dissociation into Hg^{2+} and S^{2-} only. How many ions of Hg^{2+} are there per liter? Interpret this answer (L8).

Ans. $2.9 \times 10^{-26} M$; 0.00049.

S2. The solubility product of $BaSO_4$ is calculated by a worker from a measurement of the barium ion concentration built up in a solution which is saturated by contacting 50 ml of water with 3.00 g of pure $BaSO_4$. Suppose that the pure $BaSO_4$ contains 0.010% of Na_2SO_4 as an impurity carried over from its preparation, and that this Na_2SO_4 goes quantitatively into solution during the saturation process. (a) Calculate $[Ba^{2+}]$ in the saturated solution, assuming that the solubility-product principle holds, and taking 1.00×10^{-10} for the solubility product. (b) Calculate the solubility product as the worker would by assuming it to be equal to $[Ba^{2+}]^2$, and

express the error in this value. (c) Tell how to perform this experiment to reveal such error if it is present, and to eliminate it.

S3. The solubility product of BaSO_4 is to be found in $0.0010\text{ }M$ NaIO_3 from a measurement of the concentration of Ba^{2+} built up in a solution which is saturated by contacting 50 ml of water with 3.00 g of pure BaSO_4 . Suppose that the iodate is adsorbed slightly by surface exchange, enough to liberate 0.010% of the sulfate into the solution. Answer the questions posed in Prob. S2.

Ans. (a) $0.34 \times 10^{-5}\text{ }M$; (b) 0.12×10^{-10} ,
only about 12% of the true value.

S4. For the illustrative example on page 710, show that the solubility product of $\text{Mn}(\text{OH})_2$ is not exceeded. Apply a similar test to show that the acid ionization of Mn^{2+} is not important.

S5. In Appendix V, the solubility product for AgOH is given as 1.0×10^{-8} , and the acid ionization constant for Ag^+ is given as 10^{-10} . Show that these two values require that the concentration of undissociated AgOH be $10^{-4}\text{ }M$ in the saturated solution.

S6. A $0.30\text{ }M$ NaClO_4 solution is saturated with pure $\text{Pb}(\text{IO}_3)_2$ and the concentration of lead in solution is found to be $9.86 \times 10^{-5}\text{ }M$. A $0.30\text{ }M$ HClO_4 solution saturated with the same preparation of $\text{Pb}(\text{IO}_3)_2$ is found to contain $15.17 \times 10^{-5}\text{ }M$ lead (M17). (a) Check with Appendix VI, and show that the difference in solubilities is not due to the inert-electrolyte effect. (b) Postulate a reaction to explain the difference in solubilities. (c) Use the given data to calculate K_s and the equilibrium constant for the postulated reaction.

S7. A value of 32 mg/l has been reported for the solubility of Ag_2MoO_4 at 25°C . The workers found that the precipitate used to saturate the solution was clean, crystalline, and of the theoretical composition. They then calculated a value of 2.5×10^{-12} for the solubility product. Check their calculation. Outline the further work that you would do to find if any serious error exists in this value.

S8. Correcting for activity effects, calculate the solubility of BaSO_4 (a) in $0.010\text{ }M$ BaCl_2 , and (b) in $0.010\text{ }M$ MgCl_2 . Compare these answers with the solubility in pure water, and use them to justify the statement on page 708 that the inert-electrolyte effect is usually small compared to the common-ion effect.

S9. A worker makes a solubility measurement on the substance A_2B , and assuming complete ionization, he reports a solubility-product value of 6.0×10^{-13} . Later, another worker finds that ionization of A_2B takes place exclusively into A_2^{2+} and B^- . Recalculate the solubility product.

Ans. 2.82×10^{-9} .

THE FORMATION OF PURE PRECIPITATES

MECHANISM OF PRECIPITATE FORMATION

Supersaturation and Nucleation (K8, V1)

(See Sec. 12B.2, p. 179)

Theoretical progress is being made in expressing the dependence of rate of nucleation upon the degree of supersaturation. Two types of theoretical equations have been proposed, both of which are supposed to fit the rate curve of Fig. 12.3 (p. 181).

$$V = ae^{-b}/(\log \alpha)^2 \quad (\text{Becker-Doering}) \quad (Sa)$$

$$V = kC^n = k'\alpha^n \quad (\text{Christiansen-Nielsen}) \quad (Sb)$$

$$\alpha = C/S \quad (Sc)$$

In these equations, V is the rate of formation of nuclei. The parameters a , b , k , and k' depend upon temperature and other characteristics of the solute-solvent system. The *degree of supersaturation*, α , is the ratio of the concentration of the solution to the concentration of the saturated solution. In Eq. *Sb*, n represents the number of molecules per nucleus. For ionic precipitates, values of n ranging from 3 to 10 have been reported. (The equations are also applicable to transitions in other systems. Thus, for condensation in vapor-liquid systems, the size of the nucleus is usually less than 100 molecules, corresponding to droplet diameters around 10 Å.)

In nucleus formation, it is postulated that aggregates of molecules below the critical nuclear size are unstable, possibly because they contain too few molecules to permit establishment of the attractive forces that hold the array together in a bulk-sized crystal. Even when such subnuclear aggregates are accidentally formed, they are unstable and dissociate. For a stable nucleus to form, therefore, a simultaneous aggregation of many molecules is required:



The rate of such a process would depend upon the n th power of the concentration, if it did not occur stepwise. Experimental verification of nucleation theories has not been successful. One of the main difficulties has been *heterogeneous nucleation* on particles other than nuclei of the pure substance. The importance of heterogeneous nucleation has been shown by repeated observation that nucleation rates are critically dependent on reagent histories, container surfaces, and traces of impurities (B10, N2).

Microscopic Picture of the Growth of Crystals

(See Sec. 12B.3, p. 181)

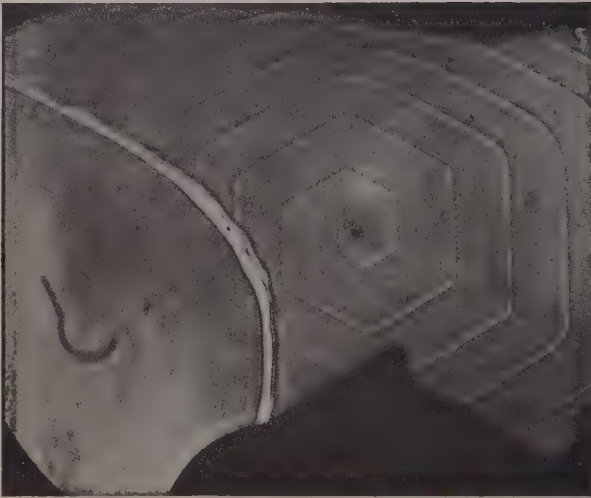
The elementary growth picture is of course an oversimplification, for it gives only an average rate of solute precipitation over all of the crystal surfaces in contact with the solution. Actually, the process is complex, and some aspects are not understood. The very fact that crystals have shapes other than spherical proves that different faces grow at different rates.

It has been well established that crystal faces do not grow by random deposition of solute molecules on the plane faces. Figure S12.1 shows spiral *growth patterns* for silicon carbide and for n -hectane, a paraffin hydrocarbon. Deposition of the solute occurs at the step edges, and the spiral propagates along its axis as growth proceeds. Step heights correspond to the height of a unit crystallographic cell, as obtained from X-ray measurements, or to some simple multiple of this height, indicating that the layers are just 1 or 2 molecules thick.

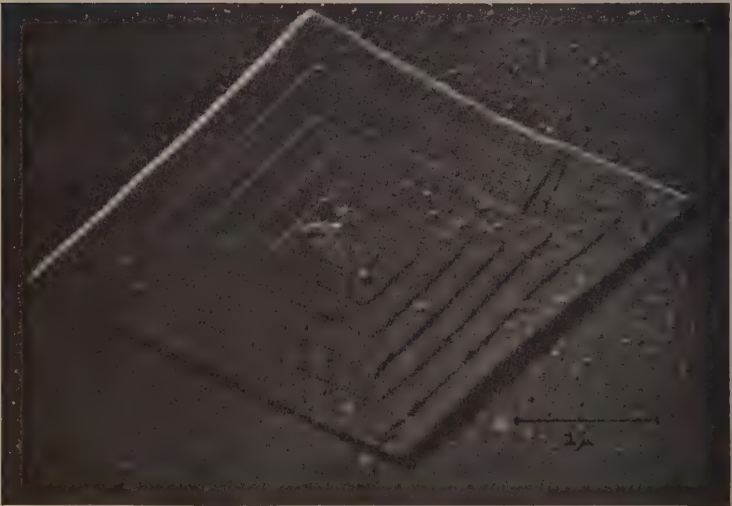
It has also been shown that surface molecules are highly mobile, which means that a condensing molecule does not have to strike precisely at a step edge to become fixed there. Instead, it may strike at a considerable distance from the step edge and then migrate to the binding site. Thus, even though growth occurs only at step edges and imperfections, the whole surface is still available for deposition. Such migration must be invoked to explain the rapid growth of the points of whisker-like crystals, since the point areas are miniscule. Similar growth steps—not always spiral—have been observed for many other kinds of ionic and non-ionic compounds.

Another deviation from the simple unimolecular picture of growth given on page 181 is that the rate has been reported to show second and even higher order dependence on the degree of supersaturation.

Lastly, the condition of the surface has an effect on growth rate not provided for in the simple theory. Thus, traces of dyes, polyelectrolytes, or other impurities not only affect the growth rate profoundly, but may even alter the crystal habit or form (B28). These effects are sometimes noticeable at very low concentrations of impurity ($1:10^5$). It was dis-



(a)



(b)

FIG. S12.1. (a) Hexagonal Growth Spiral of Silicon Carbide (with phase contrast microscope, $\times 90$). (b) Growth Spiral of *n*-heptane, $C_{100}H_{202}$ (with electron microscope, $\times 10,000$). (Reprinted from A. R. Verma, *Crystal Growth and Dislocations* [London: Butterworths Scientific Publications, 1953], Figs. 17 and 29, by permission of the publisher.)

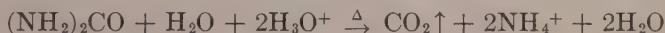
covered very long ago that urea causes common salt to crystallize as octahedral crystals instead of the usual cubic ones. These observations seem logical: it takes very little adsorbed impurity to cover the surface of a growing crystal with a monolayer, which completely changes the properties of the surface, and which could therefore change the growth rate and pattern tremendously.

Homogeneous Precipitation (G4)

(See Sec. 12B.4, p. 181)

Whenever a precipitant solution is added to a solution of the substance to be precipitated, locally high degrees of supersaturation may be built up, giving a poorly formed and impure precipitate. To keep the degree of supersaturation low throughout the process, the precipitant may be generated homogeneously by means of a chemical reaction.

For example, urea may be used as a homogeneous precipitant for ferric or aluminum ions. Urea itself is so weak a base that it does not precipitate Fe^{3+} or Al^{3+} . It does not hydrolyze appreciably at room temperature, but it hydrolyzes when heated to give an increase in $p\text{H}$.



A typical procedure consists of adding a suitable amount of urea to an acidified solution of the metal ion—say Al^{3+} . A weak acid, such as formic or acetic, is also added to provide buffering action, so that the $p\text{H}$ will not rise rapidly as the urea hydrolyzes. The solution is then simply heated until the $p\text{H}$ rises to the desired value, which is around 4 for quantitative precipitation of $\text{Al}(\text{OH})_3$.

Homogeneously precipitated $\text{Al}(\text{OH})_3$ is superior to that precipitated by addition of NH_3 . It is more dense, compact, and more easily filterable. It is also much purer. Thus, 100 mg of Al^{3+} in the presence of 50 mg of Cu^{2+} carries around 40% of the Cu^{2+} when precipitated by addition of NH_3 . When done homogeneously in the presence of 1 g of Cu, less than 0.01% of the Cu^{2+} is carried.

A good number of other metal hydroxides may be similarly precipitated, with similar advantages. Other homogeneous precipitants have been developed, such as dimethyl sulfate for the generation of $\text{SO}_4^{=}$, and thioacetamide for production of H_2S .

ADSORPTION OF MOLECULES ON IONIC PRECIPITATES

(See Sec. 12C.2, p. 185)

The mechanism given on page 186 needs only a little modification to accommodate adsorption of neutral molecules as well as ions.

Many molecules are *dipoles*—that is, the center of positive charge does not coincide with the center of negative charge. Examples are H_2O , CO , SO_2 , acetic acid ($\text{CH}_3\cdot\text{COOH}$), chloroform (CHCl_3). The whole molecule is neutral, but as it approaches a surface ion, it becomes oriented with one of its ends attracted to the surface ion and the other end repelled. There will be a net attractive force, because the attracted end is closer to the surface ion than the repelled end. Mysels (M25) shows very simply that the net attractive force varies inversely as the cube of the distance between the surface ion and the nearest end of the dipole, in contradistinction to the inverse square relationship for a point charge.

Even a nonpolar molecule, whose centers of positive and negative charge coincide (i.e., CCl_4), experiences some electrostatic force of attraction, because the molecule is deformable. In coming near a surface ion, the molecules become distorted, the positive and negative centers of charge being displaced from their original positions, and a dipole moment is induced in the molecule. The attraction of an induced dipole falls off very rapidly with distance, an inverse seventh-power relationship having been shown theoretically.

In general, electrostatic forces are much less important than van der Waals and chemical forces in the adsorption of molecules.

COAGULATION OF COLLOIDS

(See Sec. 12C.4b, p. 194)

Hydrophobic Colloids

Even though the ions of an electrolyte are not primarily adsorbed, it may still be very effective in a nonspecific way in coagulating a hydrophobic colloid. As the ionic strength of the solution increases, the thickness of the counter-ion layer decreases, and repulsion between the charged colloidal particles decreases, permitting easier collision and coagulation.

The Schulz-Hardy rule states that (1) the ion that effects the coagulation (i.e., the effective ion) is the ion opposite in charge to the charge on the colloidal particles, and (2) the coagulating efficiency of an electrolyte increases rapidly with the charge on the effective ion. Typical data in support of this rule are given in Table S12.1 (W8). It may be seen that electrolytes fall roughly into four groups, as far as coagulating efficiency is concerned, according to the charge on the effective ion: quadrivalent > trivalent > bivalent > univalent. For negative sols, the cation is the effective ion; for positive sols, the anion is the effective ion.

TABLE S12.1
COAGULATION VALUES OF SALTS FOR HYDROPHOBIC COLLOIDS*†

NEGATIVE COPPER FERROCYANIDE SOL		POSITIVE FERRIC OXIDE SOL	
Salt	Coagulation Value (mmoles/l)	Salt	Coagulation Value (mmoles/l)
Th(NO ₃) ₄	0.038	K ₄ Fe(CN) ₆	0.067
Ce(NO ₃) ₃	0.034	K ₃ Fe(CN) ₆	0.096
Al ₂ (SO ₄) ₃	0.058		
Ba(C ₂ H ₃ O ₂) ₂	0.445	K ₂ Cr ₂ O ₇	0.188
BaCl ₂	0.458	K ₂ tartrate.....	0.200
SrCl ₂	0.538	K ₂ SO ₄	0.219
MgSO ₄	0.760	K ₂ C ₂ O ₄	0.238
		K ₂ CrO ₄	0.325
KCl.....	35.6	KIO ₃	0.900
NaCl.....	92.5	KBrO ₃	31.3
		KSCN.....	46.9
		KCl.....	103.1
		KClO ₃	115.6
		KNO ₃	131.2
		KBr.....	137.5
		KI.....	153.6
		K formate.....	172.5

*Data taken from H. B. Weiser, *Colloid Chemistry*, 2d ed. (New York: Wiley, 1949), Tables 50 and 51, with permission of the publisher.

†The coagulation value is that concentration of salt required to bring about coagulation of a "standard" sol under specified conditions. The more effective the coagulant action of the salt, the lower is its coagulation value.

An electrolyte may also exert a specific coagulating influence on a hydrophobic colloid. Electrolytes with adsorbable ions of charge opposite to that of the colloid tend to coagulate it, while adsorbable ions of like charge tend to stabilize the colloid. If the ions are highly adsorbable, the electrolyte may be effective as a coagulant at very low concentrations.

A moderate amount of an electrolyte may cause coagulation, but a large excess may reverse the coagulation and reform the colloid. The way in which this occurs is illustrated in Fig. S12.2 for the coagulation of a gold sol (W8). When no coagulating electrolyte is added, a gold sol is negatively charged, owing to adsorption of Cl⁻ from the HCl solution in which the sol is formed. When Th(NO₃)₄ is added, Th⁴⁺ is adsorbed, neutralizing the charge on the sol and causing coagulation. As the electrolyte concentration is increased, adsorption of Th⁴⁺ increases, and eventually a stable, positively charged colloid is formed. But for very high concentrations of Th(NO₃)₄, the diffuse ion layer is so compressed that the repulsion between charged particles is much decreased, and coagulation again occurs.

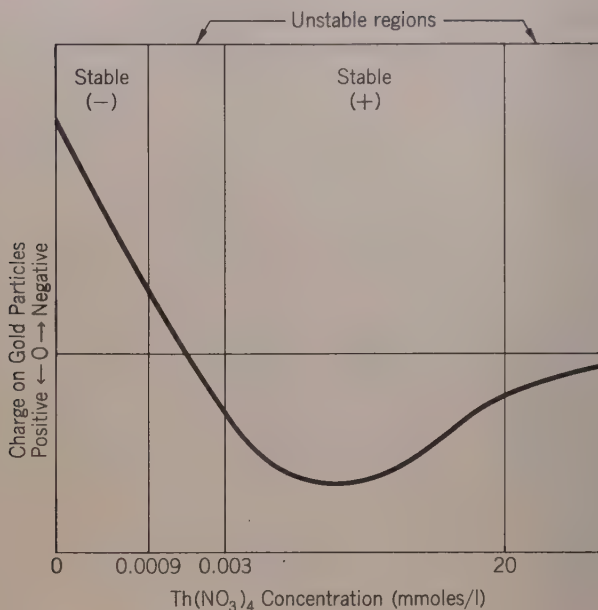


FIG. S12.2. Action of $\text{Th}(\text{NO}_3)_4$ on a Gold Colloid—The concentration scale is not linear. (Data taken from H. B. Weiser, *Colloid Chemistry*, 2d ed. [New York: Wiley, 1949], Fig. 78, with permission of the publisher.)

Similar reversals are noted with AgBr sols (**M10**). Thus, a sol containing about 2×10^{-4} moles of AgBr per liter is: (1) coagulated if there is no excess of either KBr or AgNO_3 , (2) stabilized by an excess of 0.002 M KBr , (3) coagulated by an excess of 0.1 M KBr .

Addition of electrolytes is not the only way to effect coagulation of hydrophobic colloidal particles. Nonelectrolytes, such as alcohol or acetone, when added to aqueous solutions, decrease the dielectric constant, and thereby decrease the repulsion among like-charged particles; such nonelectrolytes frequently promote coagulation of hydrophobic colloids. Also, colloids of opposite charge may mutually coagulate each other when mixed; the oppositely charged colloidal particles attract each other, forming mixed agglomerates that settle out.

Hydrophilic Colloids

Hydrophilic colloids may be coagulated by electrolytes, but high concentrations are required, and the mechanism of coagulation differs from that in hydrophobic colloids. The ions of the electrolyte remove water from the gel, which then coagulates. The order of efficiency of ions as

coagulants is roughly the same as their order of hydration. Dehydration and coagulation may also be brought about by adding a nonaqueous solvent such as alcohol or acetone to decrease the water content of the dispersed phase and to cause coagulation.

CONTAMINATION OF PRECIPITATES

Examples of Contamination by Compound Formation

(See Sec. 12D.1a, p. 195)

A *double compound* is composed of two compounds, united in simple and definite proportions. The crystal form, solubility, and other properties may differ greatly from the properties of the component compounds. Examples are given in the following paragraphs.

A double compound formed from electrolytes has identity only in the solid state: when dissolved, it dissociates into its component ions.

When formed by precipitation from a solution or from a melt, the composition of the double compound is independent of the ratio of the concentrations of the component compounds in the solution, sometimes over a rather wide range of variation in concentrations. Constancy of composition distinguishes double compound formation from mixed crystal formation by isomorphic substances.

The host may form a double compound with an impurity. For example, PbF_2 may be precipitated by adding a solution of $\text{Pb}(\text{NO}_3)_2$ to a solution of NaF . If, however, the NaF solution also contains NaCl , the less soluble compound $\text{PbF}_2 \cdot \text{PbCl}_2$ may be precipitated over a range of NaF and NaCl concentrations before the solubilities of either pure PbF_2 or pure PbCl_2 are exceeded. Pure PbF_2 (or pure PbCl_2) is not obtained except at very low concentrations of NaCl (or NaF). In fact, the composition of the double compound remains constant over such a wide range of NaCl and NaF concentrations that it is the basis of a gravimetric method for the determination of fluoride.

The host compound may form a double compound with a reagent. For instance, insoluble $\text{La}_2(\text{C}_2\text{O}_4)_3$ is formed on the addition of a solution of $\text{K}_2\text{C}_2\text{O}_4$ to a solution of LaCl_3 . However, the double compound $\text{La}_2(\text{C}_2\text{O}_4)_3 \cdot \text{K}_2\text{C}_2\text{O}_4$ is moderately insoluble, and the $\text{La}_2(\text{C}_2\text{O}_4)_3$ first formed may be metathesized to the double compound on the addition of only a moderate excess of $\text{K}_2\text{C}_2\text{O}_4$ (K12). Similar compounds are also formed by $(\text{NH}_4)_2\text{C}_2\text{O}_4$ and $\text{Na}_2\text{C}_2\text{O}_4$.

Occasionally, the sought-for substance may react with the reagent to give a compound other than the sought-for host compound, in which case the host becomes contaminated with the other compound. This happens in the formation of hydroxides of many metal ions. Almost all

metal ions except the alkalis and alkaline earths tend to hydrolyze and form basic salts having rather low solubilities. Thus Pb^{2+} forms PbOHNO_3 , Hg^{2+} forms HgOHNO_3 , Al^{3+} forms $\text{Al}(\text{OH})_2\text{Cl}$ and AlOHCl_2 , etc. An attempt to precipitate pure $\text{Al}(\text{OH})_3$ from a solution of AlCl_3 by adding NH_3 may lead to local formation of the basic salt during the precipitation process. If the basic salt is covered over by subsequently formed precipitate, it may not be metathesized to $\text{Al}(\text{OH})_3$ after excess NH_3 is added; this metathesis can occur only if the excess NH_3 can reach the basic salt. Basic salt formation instead of pure hydrous oxide formation usually causes no error in gravimetric analysis because the salts are all decomposed and converted to the oxides upon ignition. On the other hand, it is because of the formation of basic salts that most metal ions cannot be accurately and reproducibly titrated with standard base to form insoluble hydroxides.

Distribution of Isomorphically Carried Impurities (W2)

(See Sec. 12D.1b, p. 199)

There are two ideally extreme ways in which an isomorphic impurity may be coprecipitated with the host, each resulting in a different distribution of the impurity throughout the host.

If the precipitate comes into equilibrium with the solution, the coprecipitated impurity (I) is distributed evenly and homogeneously throughout the host (H), as in Fig. 12.6a (p. 200), according to the following equilibrium:



If D is the equilibrium constant, the equilibrium expression may be written and rearranged to describe the impurity distribution quantitatively.

$$D = \frac{[H]_{\text{soln}}[I]_{\text{ppt}}}{[H]_{\text{ppt}}[I]_{\text{soln}}} \quad (\text{Sb})$$

$$\frac{[I]_{\text{ppt}}}{[H]_{\text{ppt}}} = D \frac{[I]_{\text{soln}}}{[H]_{\text{soln}}} \quad (\text{Sc})$$

In Eq. *Sc*, the bracketed terms represent concentrations (or better, activities) in any convenient concentration units in the designated

*Only the isomorphic case is considered here, in which I has the same charge as H , and replaces it mole for mole in the precipitate. If the charge on I is different from the charge on H , the concentration ratios in Eq. *Sc* are exponentially related rather than linearly.

phases. Since in any one phase the ratio of the concentrations is the same as the ratio of the amounts, Eq. *Sc* may also be written:

$$\frac{(\text{wt. of } I)_{\text{ppt}}}{(\text{wt. of } H)_{\text{ppt}}} = D \frac{(\text{wt. of } I)_{\text{soln}}}{(\text{wt. of } H)_{\text{soln}}} \quad (Sd)^*$$

The impurity distribution represented by Eqs. *Sc* and *Sd* is called a *homogeneous, equilibrium, or Nernst distribution*. Equilibrium distributions have been observed in very slow and carefully controlled precipitations, usually followed by long digestion periods. Since equilibrium is established very slowly in the solid phase, Eqs. *Sc* and *Sd* are idealized equations that are seldom approached in ordinary precipitation processes.

According to the views of Doerner and Hoskins, equilibrium exists at any instant only between the surface layer of the precipitate and the solution. As the host crystal grows and adsorbs impurity, it becomes covered over, and the new surface formed must come into a new equilibrium with the solution. Since the host and impurity are not removed at the same rates from solution, the composition of the solution changes during the growth process, and therefore so does the composition of the surface layer. A nonuniform distribution of impurity results (see Fig. 12.6b, p. 200), which is called a *Doerner-Hoskins, heterogeneous, logarithmic, or nonequilibrium distribution*.

A quantitative expression for the distribution may be derived by assuming that the homogeneous law (Eq. *Sd*) holds during any time interval over which the composition of the solution remains constant. Let I_{ppt} and H_{ppt} represent the amounts of impurity and host that have been deposited, and let I_0 and H_0 represent the initial (i.e., total) amounts present before precipitation begins. Let dI_{ppt} and dH_{ppt} represent the amounts precipitated in the surface layer during the time interval over which the composition of the solution remains constant. Then Eq. *Sd* becomes

$$\therefore \frac{dI_{\text{ppt}}}{dH_{\text{ppt}}} = \lambda \frac{I_0 - I_{\text{ppt}}}{H_0 - H_{\text{ppt}}} \quad (Se)$$

*In the case that I is at trace levels, the solid phase is practically pure H , and $[H]_{\text{soln}}$ is practically constant, since it applies to the saturated solution. In this case, Eq. *Sd* becomes identical in form to the Freundlich equation (p. 189) for the case that $n = 1$:

$$\frac{(\text{wt. of } I)_{\text{ppt}}}{(\text{wt. of } H)_{\text{ppt}}} = k[I]_{\text{soln}}$$

Therefore, a simple study of how the distribution of I depends on its concentration does not serve to differentiate homogeneous isomorphic coprecipitation from adsorption or any other mechanism that follows the empirical Freundlich equation. Such differentiation requires a more critical study.

Integration gives

$$\log \frac{I_0}{I_0 - I_{\text{ppt}}} = \lambda \log \frac{H_0}{H_0 - H_{\text{ppt}}}, \text{ or} \quad (Sf)$$

$$\log \frac{\text{total wt. of } I}{\text{wt. of } I \text{ in soln.}} = \lambda \log \frac{\text{total wt. of } H}{\text{wt. of } H \text{ in soln.}} \quad (Sg)$$

The heterogeneous distribution is approached in practice in precipitations carried out not too slowly in well-stirred solutions.

The concentration dependences of the homogeneous and heterogeneous distributions are definitely different, and may be used to differentiate between the two mechanisms. To find which mechanism a particular case follows, the fraction of impurity carried is measured as a function of the fraction of the host precipitated. That mechanism is then assumed to be correct which gives the most constant value of D or λ over the whole range that has been studied.

Several conclusions may be drawn from Eqs. *Sd* and *Sg*:

1. A value of D or λ greater than unity means an enrichment of the impurity in the solid phase, while a value less than unity signifies a depletion. There have been attempts to relate D and λ to the ratio of the solubility products of the impurity and host compounds, but success has been indifferent. Roughly, the less soluble compound tends to concentrate in the solid phase. Figure S12.3 shows how efficiently the impurity is coprecipitated for various values of D or λ .

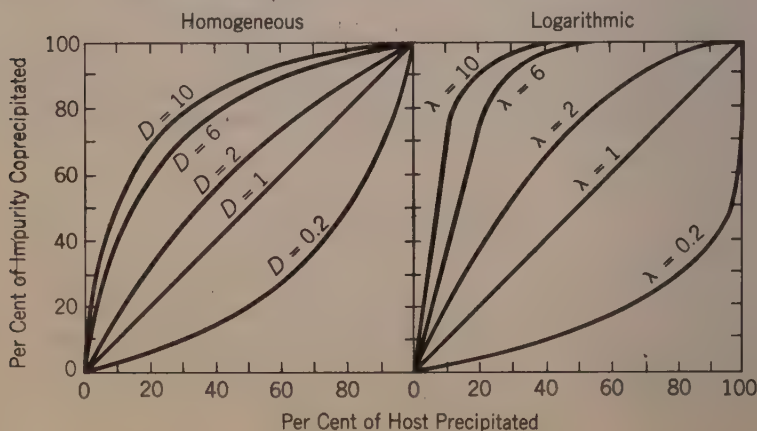


FIG. S12.3. Coprecipitation of Isomorphous Impurities for Various Values of D and λ . (Data taken from Arthur C. Wahl and Norman A. Bonner, *Radioactivity Applied to Chemistry* [New York: Wiley, 1951], Fig. 6.8, with permission of the publisher.)

2. Any condition favoring complete precipitation of the host (which is always an objective in gravimetric analysis) also favors efficient coprecipitation of the impurity. Conversely, any attempt to draw the isomorphically coprecipitated impurity from the precipitate back into solution will also cause the sought-for substance to redissolve. In other words, the removal of an isomorphically coprecipitated impurity cannot be achieved by the simple measures that are effective for surface-adsorbed impurities.

It should be pointed out that isomorphic coprecipitation does not occur if the isomorphs are of greatly differing solubilities. Thus NaCl and AgCl are cubic isomorphs, miscible in all proportions, with lattice spacings of 5.63 and 5.55 Å, respectively. Yet AgCl precipitated from a NaCl solution is negligibly contaminated with NaCl. Because of the comparatively high solubility of NaCl, D is very low, and NaCl is distributed inappreciably into the solid phase. Similarly, although KMnO_4 is isomorphic with BaSO_4 , and although the lattice spacings are quite similar, BaSO_4 formed in rather concentrated KMnO_4 solutions carries only enough KMnO_4 to impart a faint pink color to the precipitate.

Eqs. S_d and S_g would also be expected to hold for the coprecipitation of nonisomorphic impurities, but only over that range in which the impurity is coprecipitated as a true solution in the host precipitate. If the impurity and host ions do not have the same charge, then the distribution equations are more complicated than Eqs. S_d and S_g .

Coprecipitation of many substances on a wide variety of hosts has been reported in the literature. Wahl and Bonner (W2) summarize data for many systems.

Supersolubility of Small Particles

(See Sec. 12D.2c, p. 203)

The solubility of small particles is described on page 705. The general dependence of solubility upon particle size is given, and solubilities are calculated for some of the more common precipitates.

The supersolubility of small crystals explains the slow growth and perfection of large crystals at the expense of smaller ones. A principal purpose of digestion is to allow time for this process to occur. Elevated temperature is often used to hasten the formation of large crystals.

Figure S12.4 is a plot of S_r/S against r for BaSO_4 and AgCl , calculated from the equation on page 706. From this figure, it is easy to see how BaSO_4 crystals might grow rapidly during digestion, since small particles are so much more soluble than large ones. On the other hand, AgCl crystals might not be expected to grow rapidly, since the large and small particles differ little in solubility. These solubility characteristics may

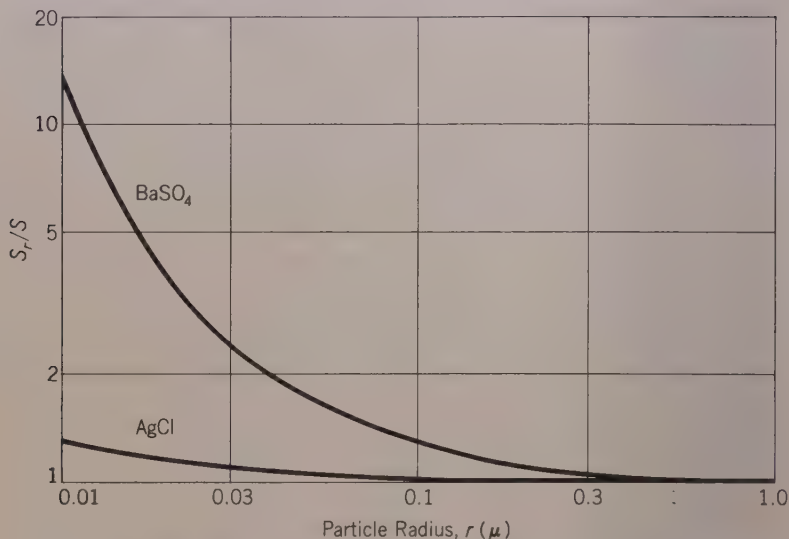


FIG. S12.4. Dependence of Solubility upon Particle Size for BaSO_4 and AgCl (25°C)—The solubilities are calculated, using γ for BaSO_4 as 1250 dynes/cm and an estimated γ of 250 dynes/cm for AgCl , from Table S11.1 (p. 706).

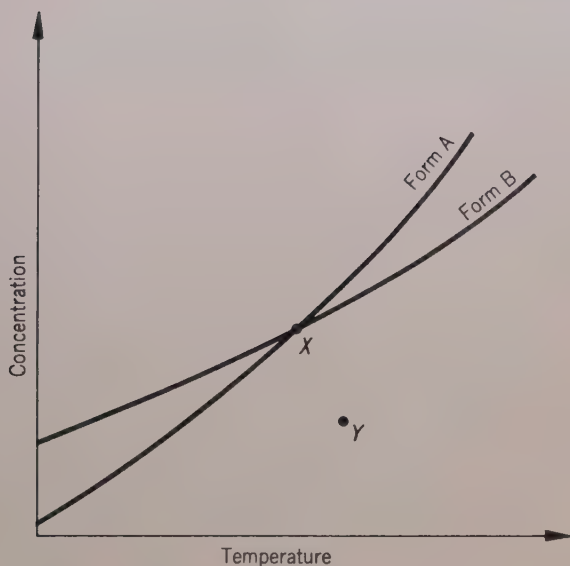
be used to explain the difference in character between the microcrystalline BaSO_4 and the curdy AgCl precipitates.

Early work on the importance of supersolubility during digestion and aging is controversial. Recently, May and Kolthoff (M11) showed that freshly precipitated PbCrO_4 with particle diameters around 0.2μ had a solubility around 70% higher than that of the bulk crystals, and that this supersolubility disappeared rather quickly upon aging. However, there is much evidence that suggests that the supersolubility of small particles is not of primary importance in the digestion and aging of many precipitates.

SUPPLEMENTARY QUESTIONS

Section 12B

- S1. In Eqs. S_a and S_b (p. 716), in what units might the rate, V , be expressed?
- S2. The accompanying figure gives the solubility curves for two polymorphic forms of the same substance. (a) What is the point X called? (b) If an unsaturated solution is cooled until crystallization occurs, define conditions under which Form B will be obtained as the stable form, and also define conditions under which Form A will be obtained as the stable form. (c) Repeat part b for an evaporative process at constant temperature.



S3. (a) Starting with a solution represented by point *Y* in the accompanying figure, tell how to process the solution to obtain Form A as the stable form. (b) Repeat part *a*, to obtain Form B as the stable form. (c) Explain how there is a probability of obtaining Form B as a metastable form in the process of part *a*, and also of obtaining Form A as a metastable form in the process of part *b*.

S4. A differential equation for the growth of crystals is:

$$\frac{dC}{dt} = -kA \frac{C - S}{S}$$

C is the actual solute concentration, while *S* is its solubility, or saturation concentration. *A* is the surface area on which growth occurs, and *k* is a proportionality constant. Dissolution is represented by the same equation since at undersaturation, $C < S$. However, for a particular substance, *k* for the dissolution may be orders of magnitude greater than for growth. Explain.

S5. Write chemical equations to show the homogeneous generation of sulfate by dimethyl sulfate, and of H_2S by thioacetamide.

S6. In a solution containing excess BaCl_2 , suppose that sulfate is produced homogeneously at a constant rate, by the reaction



Draw rough plots, showing qualitatively how $[\text{SO}_4^{2-}]$ and $[\text{Ba}^{2+}]$ vary with time (L3).

Section 12C

S1. According to the Freundlich equation, the adsorption increases without limit as the concentration of an adsorbable substance increases. Explain why this interpretation is unreasonable.

S2. How would you determine experimentally whether or not a particular adsorption process follows the Freundlich equation?

S3. Explain why a precipitate may peptize when washed, and why addition of an electrolyte to the wash solution may prevent such peptization.

S4. Explain why a little electrolyte in the wash water may be effective in preventing peptization, whereas a lot might be ineffective.

S5. Why are there fairly wide variations in coagulating efficiencies among salts of the same type in Table S12.1 (p. 721)?

S6. (a) For the AgBr sol described on page 722, explain the mechanisms responsible for stabilization or coagulation at various KBr concentrations. (b) On addition of 2 *M* KBr, a clear solution results that cannot be coagulated by shaking or heating. Explain.

Section 12D

S1. Describe how a trace of each of the following radioactive ions might be carried efficiently upon an inactive carrier precipitate that contains no inactive isotope of the desired radio-element. (Thus radio- Cl^- should not be carried by inactive AgCl.) (a) Cl^- , (b) CrO_4^{2-} , (c) Ba^{2+} , (d) PO_4^{3-} , (e) Cd^{2+} .

S2. Traces of the following pairs of radioactive ions may exist in the same solution. Explain how separation might be accomplished in each case by carrying one member of the pair on an inactive carrier precipitate, leaving the other member in solution. (a) Cl^- , SO_4^{2-} ; (b) Pb^{2+} , Bi^{3+} ; (c) Ba^{2+} , Fe^{3+} ; (d) NO_3^- , Cl^- ; (e) CO_3^{2-} , SO_4^{2-} .

S3. A trace of radio- Pb^{2+} is to be coprecipitated efficiently with $\text{Ag}_2\text{C}_2\text{O}_4$. Outline the method of precipitation that would give maximum yield of Pb^{2+} in the precipitate.

S4. Outline an experiment that would permit a statement as to whether or not a particular case of contamination occurs by adsorption or by isomorphic coprecipitation.

S5. For the homogeneous isomorphic coprecipitation of Pb^{2+} on $\text{Ba}(\text{IO}_3)_2$, *D* is reported to be 25. (a) Which is more insoluble: $\text{Pb}(\text{IO}_3)_2$ or $\text{Ba}(\text{IO}_3)_2$? (b) Explain what inferences may be made regarding the value of *D* for the coprecipitation of Ba^{2+} on $\text{Pb}(\text{IO}_3)_2$.

SUPPLEMENTARY PROBLEMS

Section 12B

S1. Assuming that *S* is about 1.25×10^{-5} *M* for all sizes of BaSO_4 crystals, compute and check some of the degrees of supersaturation in Table 12.1 (p. 183).

S2. What is the degree of supersaturation of a 0.00014 *M* AgCl solution at each of the following temperatures: 25, 50, 75, 100°C? (See Fig. 11.1, p. 162, for solubilities.)

S3. In the following pairs of figures, the first number represents the degree of supersaturation (α), and the second represents the rate of nucleus formation (number generated per cc per second) for cyclonite (a cyclohexane derivative) when crystallized from an acetone- HNO_3 solution (V1, p. 179): 2.87–380, 2.90–970, 2.85–1160, 3.37–4370, 3.80–4680, 4.66–19,500, 5.14–24,100, 5.75–75,000. Assuming that the Christiansen-Nielsen theory best fits the data, find the nuclear size. (Hint: Plot $\log V$ against $\log \alpha$.) Ans. About 6.

S4. Examine the Becker-Doering and the Christiansen-Nielsen nucleation equations (p. 716) to find how well they really fit a rate curve like that of Fig. 12.3 (p. 181). (Hint: Examine the slopes, $dV/d\alpha$, as α approaches unity and infinity.)

S5. The degree of supersaturation as defined on page 716 serves well when only one un-ionized solute species is involved. In the case of an ionic precipitate, like AgCl, this simple definition of α breaks down. Thus, supersaturation can be high not only

in solutions containing equivalent concentrations of Ag^+ and Cl^- , but also in solutions containing high Ag^+ and low Cl^- , or high Cl^- and low Ag^+ . Devise a more appropriate definition of α for AgCl , and check in the literature (v1).

$$\text{Ans. } \alpha = ([\text{Ag}^+][\text{Cl}^-]/K_s)^{1/2}.$$

Section 12C

S1. In the following pairs of figures, the first number is the milligrams of Na occluded per 2.00 g of BaSO_4 , and the second number is $[\text{Na}^+]$ (in moles per liter) existing in the mother liquor during formation of the BaSO_4 (R10). Discover if the Freundlich equation holds by plotting the log of the milligrams of Na carried against $\log [\text{Na}^+]$, and drawing the best straight line possible through the points. Evaluate k and n from the intercept and slope. 2.7–0.049, 5.6–0.293, 6.1–0.538, 7.9–1.03, 10.2–1.52, 12.4–2.49, 15.4–3.47, 14.8–4.94.

$$\text{Ans. } k = 4.2 \text{ mg/g, } n = 2.6.$$

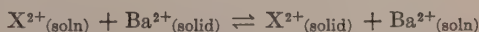
S2. In the following pairs of figures, the first number is the milligrams of Mn carried per 346 mg SnO_2 , and the second number is the total milligrams of Mn present (G3). The host SnO_2 is always thrown down at pH 1.5 from a constant volume of solution. Note the high coprecipitation of Mn, even though MnO_2 does not precipitate alone until pH 8.5 is reached, and even though the SnO_2 is washed with 15 portions of water. Does the Freundlich equation apply to these data? If so, calculate k and n . 0.33–1, 0.9–10, 1.35–50, 1.85–100, 2.3–200, 2.5–300.

S3. Let b be the distance of separation between the positive and negative centers of charge in a dipole, and let a be the distance between the oriented dipole and a surface ion to which it is attracted. Let all charges be unity. Assume that $a \gg b$, and neglect the effect of other charged ions in the surface. Show that the net force attraction between the dipole and the surface ion varies as b/a^3 (M25).

Section 12D

S1. For the coprecipitation of an impurity upon an isomorphic host, $D = 0.1000$. (This is a case favorable for separation, since isomorphic substances seldom have D 's differing greatly from unity.) If a solution containing both substances is treated to precipitate 99.9% of the host, show that 99% of the impurity is coprecipitated, indicating virtually no separation between the substances.

S2. For the homogeneous coprecipitation of a trace of X^{2+} on $\text{Ba}(\text{IO}_3)_2$, $D = 3.00$ for the reaction



A system originally contains 0.00100 M $\text{Ba}(\text{NO}_3)_2$ and a trace of $\text{X}(\text{NO}_3)_2$. If 90.0% of the Ba^{2+} is precipitated as $\text{Ba}(\text{IO}_3)_2$, what percentage of the X^{2+} remains in solution?

S3. Repeat the calculation for Prob. S2, if the coprecipitation is heterogeneous, with $\lambda = 3.00$, and compare answers.

Ans. 0.100%; heterogeneous coprecipitation much more efficient.

S4. For $D = 20$ in Fig. S12.3 (p. 726), calculate the percentages of impurity carried homogeneously when 10% and 40% of the host is precipitated. Sketch the curve roughly into Fig. S12.3. Repeat the calculations for logarithmic carrying, if $\lambda = 20$.

S5. PbSO_4 is isomorphic with BaSO_4 . BaSO_4 was precipitated homogeneously from a $\text{Ba}(\text{NO}_3)_2$ solution containing a trace of $\text{Pb}(\text{NO}_3)_2$. The homogeneous precipitant was sulfamic acid. At various times, corresponding to various fractions of BaSO_4 precipitated, the precipitate was analyzed. Radiotracers Ba^{2+} and Pb^{2+} were used to lighten the analytical work (C4).

At 145 minutes, the precipitate contained 14.1% of the total Ba^{2+} and 2.86% of the total Pb^{2+} ; at 180 minutes, 30.0% of the Ba^{2+} and 6.59% of the Pb^{2+} ; at 259 minutes, 60.3% of the Ba^{2+} and 15.92% of the Pb^{2+} ; at 496 minutes, 94.12% of the Ba^{2+} and 42.39% of the Pb^{2+} ; at 1156 minutes, 99.66% of the Ba^{2+} and 63.5% of the Pb^{2+} . Calculate λ and D for these data, and state whether the coprecipitation is homogeneous or logarithmic.

Ans. $\lambda = 0.177$ to 0.195 ; $D = 0.179$ to 0.0059 ; logarithmic.

S6. The isomorphic coprecipitation of traces of Y^{3+} with $\text{Ce}_2(\text{C}_2\text{O}_4)_3$ has been studied under carefully controlled conditions (F1). When 15.0% of the Ce^{3+} is precipitated, 9.35% of the Y^{3+} is carried along; and when 91.9% of the Ce^{3+} is precipitated, 78.2% of the Y^{3+} is coprecipitated. Show that these data fit the logarithmic distribution better than the homogeneous distribution, and calculate λ and D for both experiments.

Ans. $\lambda = 0.61, 0.60$; $D = 0.59, 0.31$.

S7. Use Eq. *Sg* (p. 726) to show that when $\lambda > 1$, the impurity concentrates in the precipitate.

S8. Derive the analog of Eq. *Sd* (p. 725) for coprecipitation when the impurity ion has a charge different from that of the host. As an example, use the coprecipitation of Pb^{2+} on Ag_2CrO_4 , for which the value of D is reported to be 1.4 (W2).

S9. Compute some of the values of S_r/S from the data given in Table S11.1 (p. 706).

S10. To compute the AgCl curve of Fig. S12.4 (p. 728), a value is required for the surface tension (γ) of solid AgCl . This is not easy to find in the literature, but it may be found that the hardness of AgCl is 1.3 (Mohs' scale). Use the data of Table S11.1 to find if there is a correlation between hardness and γ . Use this correlation to estimate γ for AgCl from its hardness, and check your estimate with the value of 250 dynes/cm that was used in Fig. S12.4. Is the estimate a precise one?

GRAVIMETRIC METHODS

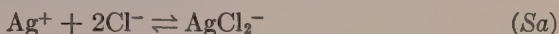
EXTENSIONS OF THE GRAVIMETRIC METHOD FOR DETERMINING CHLORIDE

(See Exp. 13.1, p. 214)

Determination of Metals That Form Insoluble Chlorides

Ag^+ and Hg_2^{2+} may be determined by the precipitation and weighing of AgCl and Hg_2Cl_2 . Pb^{2+} is not determinable in this way, since PbCl_2 is moderately soluble.

In the determination of Ag^+ as AgCl , a large excess of chloride precipitant must be avoided, since a soluble argentochloride complex is formed at high chloride concentrations.

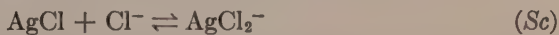


Reaction *Sa* competes with the reaction for AgCl precipitation.



Reaction *Sa* becomes relatively more important with increase in chloride concentration. Note that the mass-action effect of chloride in forcing these two equilibria to the right depends upon $[\text{Cl}^-]^2$ in reaction *Sa*, but only upon $[\text{Cl}^-]$ in reaction *Sb*.

On the addition of reaction *Sa* to the reverse of reaction *Sb*,



Thus it may be seen that AgCl redissolves if the excess chloride concentration becomes too high. Figure S13.1 shows the solubility of AgCl in NaCl solutions (**S10**). As a result of the common-ion effect, the solubility of AgCl is decreased by NaCl concentrations up to about 0.001 *M*. However, at higher NaCl concentrations, reaction *Sc* becomes increasingly important, and the solubility of AgCl increases with increasing NaCl concentration, eventually exceeding the solubility in pure water by tenfold as the NaCl concentration approaches 1 *M*. In the deter-

mination of Ag^+ as AgCl , it is therefore desirable to keep the excess chloride below a few hundredths molar.

Problems on the solubility of AgCl in solutions containing excess NaCl are given on page 744.

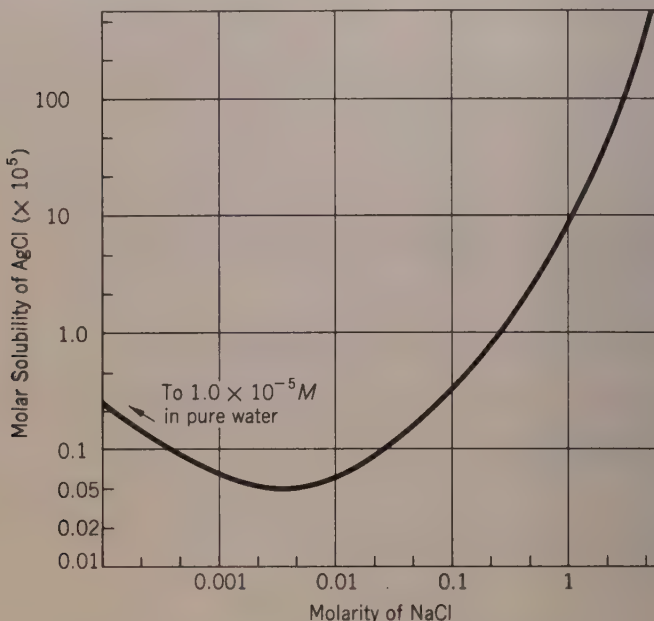


FIG. S13.1. Solubility of AgCl in NaCl Solutions

Some other metallic halides (HgI_2 , PbCl_2) also form soluble halide complexes. HgI_2 has a great tendency to form HgI_4^{2-} . Hg_2Cl_2 is also soluble in large excesses of chloride, and in addition is volatile at a lower temperature than AgCl ; hence the determination of Hg_2^{2+} as Hg_2Cl_2 tends to give low results.

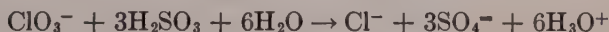
Determination of Anions That Form Insoluble Ag Salts

SCN^- , Br^- , and I^- form Ag salts insoluble in acid, and any of these is theoretically determinable by precipitation with excess Ag^+ in the absence of the others and chloride. Even anions forming acid-soluble salts (such as CN^- or PO_4^{3-}) may be so determined at sufficiently low acidities. However, the determination of most anions is more difficult than the determination of chloride. For example, the determination of iodide as AgI is passable, but not very satisfactory; iodide is oxidized more easily than chloride by HNO_3 . Also, AgI peptizes more easily than AgCl , is more photosensitive, and holds impurities more tenaciously. AgBr suffers from the same disadvantages as AgI , but less severely, and may be

determined satisfactorily. In short, the anions mentioned above are usually determined by other easier and more accurate methods, rather than gravimetrically as the Ag salts.

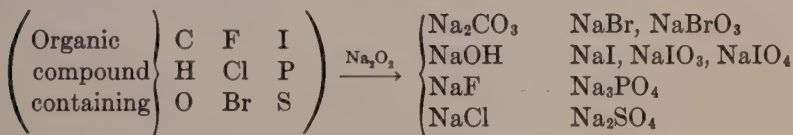
Determination of Oxyhalogen Anions

The following anions may be reduced to the halides, which may then be determined as in the preceding paragraph: ClO^- , ClO_2^- , ClO_3^- , ClO_4^- , BrO^- , BrO_3^- , IO^- , IO_3^- , IO_4^- . Various reducing agents may be used, such as HNO_2 , Fe^{2+} , Zn (metal), and SO_2 . The last reduces all the above anions except ClO_4^- , and the excess SO_2 may be expelled simply by boiling (S9). For example, the equation for the reduction of ClO_3^- is



Determination of Halogens in Organic Compounds

The halogens in organic compounds are generally bonded non-ionically, and are not precipitable as silver halides by the addition of excess AgNO_3 . It is first necessary to decompose the organic compounds. There exists a variety of methods of decomposition, one of the most popular being the *Parr oxidation*, in which the organic compound is fused under pressure in a Parr bomb with Na_2O_2 (F11). The organic material is oxidized, and halogens, sulfur, and phosphorus are converted to sodium salts as follows:



After fusion, the melt is carefully taken up in water, and the solution boiled to decompose excess Na_2O_2 . If only a single halide is present, it may be determined after acidification* of the solution. If several salts are present, separations or indirect methods must be used. Often, the halides formed are determined volumetrically instead of gravimetrically.

In the *Carius method*, the organic compound is decomposed by heating with fuming HNO_3 to 200–300°C in a sealed, heavy-walled glass tube. If the heating is done in the presence of AgNO_3 , the silver halides are formed directly and may be filtered off and weighed after reaction is complete. In yet another method, the organic compound is quantitatively burned in a stream of air, and the products are absorbed in an

*Silica, present as an impurity in the Na_2O_2 , may come down at this point, and must be filtered off before precipitation of the sought-for substance. Removal of silica may not be necessary if volumetric methods of determination are used.

H_2O_2 solution. This process converts halogens to the hydrogen halides, and sulfur to H_2SO_4 , which may be determined after excess H_2O_2 is destroyed by boiling.

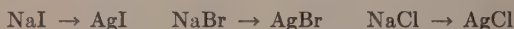
Analysis of Halide Mixtures (T2)

Mixtures of two halides may be determined in many ways by indirect analysis, based upon differences in chemical properties of the halides, which allow their separation and determination. (1) I^- may be determined in the presence of Br^- and/or Cl^- by precipitation and weighing as PdI_2 . (2) In dilute acid, HNO_2 oxidizes I^- to I_2 , which may be driven off by boiling. This allows determination of I^- by difference on two portions of a sample. From one portion, the total halides are obtained as Ag salts. From a second portion, the I^- is oxidized and expelled, and the residual halides determined as Ag salts. In this method the solution must be dilute, or there may be loss of HCl or HBr on boiling. (3) On heating with $\text{K}_2\text{Cr}_2\text{O}_7$ in conc. H_2SO_4 , AgCl and AgBr are converted to Cl_2 and Br_2 , which may be distilled off. AgI , however, is converted to iodate, which is nonvolatile and remains in the boiler along with all Ag^+ . Reduction of iodate after distillation reprecipitates AgI alone, which may then be weighed. Combination of these methods allows determination of mixtures of three halides, as shown in the following example.

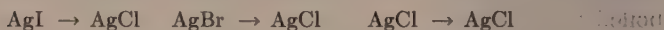
Example. A sample contains only NaI , NaBr , NaCl , and Na_2SO_4 . Describe a method of analysis for this sample, and outline the computations.

PROCEDURE. Take two portions of sample, each of weight S g.

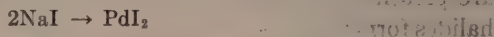
Portion 1: (a) Precipitate all halides as Ag salts, obtaining T g of precipitate.



(b) Convert the mixture of Ag halides to AgCl in a stream of chlorine, obtaining U g of precipitate.



Portion 2: Precipitate I^- as PdI_2 , obtaining V g of precipitate.



CALCULATIONS. Let x , y , and z be the weights of NaI , NaBr , and NaCl , respectively, in each original portion of S g. Then

$$T = x \frac{234.77}{149.89} + y \frac{187.78}{102.90} + z \frac{143.32}{58.44}$$

$$U = x \frac{143.32}{149.89} + y \frac{143.32}{102.90} + z \frac{143.32}{58.44}$$

$$V = x \frac{360.2}{2(149.89)}$$

These three equations allow calculation of x , y , and z from the measured quantities T , U , and V and the known molecular weights. The amount of Na_2SO_4 may be obtained by difference, $S - (x + y + z)$.

EXTENSIONS OF THE GRAVIMETRIC METHOD FOR DETERMINING SULFATE

(See Exp. 13.2, p. 221)

Determination of Cations That Form Insoluble Sulfates

The determination of Ba^{2+} is easier and more accurate than that of sulfate. Coprecipitation of H_2SO_4 when H_2SO_4 is added in excess as a precipitant to BaCl_2 causes no error, since H_2SO_4 is volatilized on ignition. In addition, solubility losses may be virtually eliminated by using dilute H_2SO_4 as a wash liquid, which cannot be done in the sulfate determination.

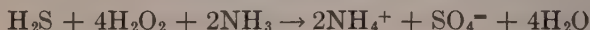
Lead may be determined as PbSO_4 , but there are difficulties, in spite of the fact that coprecipitation is less of a problem than in the case of BaSO_4 . PbSO_4 has a solubility of 40 mg/l in pure water, and an even greater solubility in dilute acid solution, so that solubility losses are appreciable. In addition, PbSO_4 is not so stable as BaSO_4 , and must not be ignited above 500°C . SrSO_4 is quite soluble (150 mg/l), and must be precipitated from and washed with alcoholic solutions to reduce solubility losses. CaSO_4 , while regarded as "insoluble" for many purposes, has too high a solubility (1 g/l) to allow accurate gravimetric determination. Ca^{2+} must be precipitated in other forms, even though CaSO_4 is a good weighing form (p. 212).

Analysis of Sulfur-Bearing Samples

Sulfur is widely distributed in natural and manufactured materials, often in oxidation states lower than sulfate. In most such materials S may be determined by oxidizing to sulfate, removing interferences, and precipitating BaSO_4 . The illustrative procedures described below are given in greater detail in analytical reference books (S9, T2). The treatment used for a given sample will depend on the nature of the sample and the oxidation state of the S.

There are three general methods for oxidizing S-bearing samples. (1) In the *wet method*, S is oxidized to sulfate with a strong oxidizing agent such as fuming HNO_3 ; Br_2 in CCl_4 , followed by HNO_3 ; $\text{HCl} + \text{HNO}_3$; $\text{HCl} + \text{Br}_2$; $\text{HNO}_3 + \text{KClO}_3$. There are disadvantages to this procedure. It is slow, giving compounds like H_2S and SO_2 a chance to escape from the acid solutions before oxidation. Also, dissolution may be incomplete, for some insoluble sulfates are not attacked. Finally, HNO_3 or HClO_3 , if used, must be removed before precipitation of

BaSO₄. The advantage of this method, however, is that the resulting solution may be used for analysis of metals in the sample as well as for S. (2) In the *dry method*, the sample is fused with an alkaline oxidizing flux (e.g., Na₂O₂ or Na₂CO₃ + KNO₃). The sample is rapidly and completely decomposed, but there are disadvantages: (a) large amounts of alkalis are introduced, increasing the coprecipitation error; (b) the flux attacks the crucible (usually Ni or Fe) in which the fusion occurs, putting indeterminate amounts of these metals into solution and rendering the solution useless for their analysis; (c) the alkaline flux strongly absorbs S-containing gases from the flame, and must be protected. An electric furnace avoids this difficulty. (3) In special cases, where the sample contains only sulfides or where only the sulfide content is desired, the sample may be treated with HCl in a nonoxidizing atmosphere (CO₂ or H₂). This process converts the sulfides to H₂S, which is evolved and absorbed in an oxidizing solution containing H₂O₂.



The excess H₂O₂ is decomposed by boiling, the solution is acidified, and then BaSO₄ is precipitated.

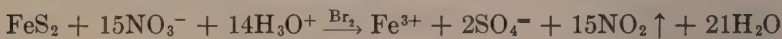
The following examples outline a few determinations for S in various kinds of samples.

1. S in inorganic compounds may be quantitatively oxidized to sulfate by several kinds of agents. NH₃ + H₂O₂ suffices to oxidize S⁻, S₂O₃⁻, and SO₃⁻. After removal of excess oxidant and acidification of the solution, BaSO₄ is precipitated. (It should be mentioned that most of the lower oxidation states of S, such as S⁻, S₂O₃⁻, and SO₃⁻, may be determined more easily volumetrically than gravimetrically.)

2. The Parr or Carius oxidation is used to convert S in organic compounds to sulfate, as described on page 735.

3. Many important ores of As, Cr, Fe, Mo, Ni, Pb, and Zn are sulfides. Wet methods of oxidation are commonly used. The analysis of pyrites (FeS₂) is typical, and is outlined in the following reactions.

(a) Oxidize and extract S from the ore.

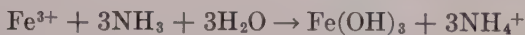


(b) Evaporate with HCl, to destroy nitrate that would coprecipitate with BaSO₄ (first reaction on p. 224).

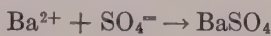
(c) Bake to render SiO₂ insoluble, since it would otherwise precipitate later with BaSO₄. (Too high a temperature causes loss of SO₃, through decomposition of sulfates.)



(d) Remove Fe^{3+} by precipitation with NH_3 , to prevent coprecipitation with BaSO_4 . Reprecipitation may be necessary to avoid loss of sulfate by coprecipitation on the $\text{Fe}(\text{OH})_3$. In some procedures, Fe^{3+} is simply reduced to less coprecipitable Fe^{2+} with metallic Zn or Al.



(e) Acidify, and precipitate BaSO_4 .



Determining S in steel is similar to determining S in pyrites, except that a milder extraction procedure suffices. Concentrated HNO_3 is a good solvent. Any Si present is oxidized to SiO_2 , which must be handled as shown above.

Analysis of Samples That Contain Insoluble Sulfates.

Na_2CO_3 Metathesis

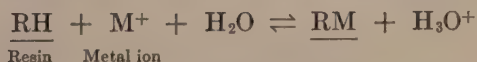
Insoluble sulfates may be metathesized to insoluble carbonates by boiling the sample with concentrated Na_2CO_3 solution, so that sulfate is put into solution.



The insoluble carbonates are filtered off, and sulfate is precipitated as BaSO_4 after acidification* of the filtrate. Certain natural or ignited materials may be unattacked by the Na_2CO_3 solution, and may require fusion with Na_2CO_3 to liberate the sulfate. The melt is extracted with water, leaving the insoluble carbonates behind and taking sulfate into solution. Such metathesis with Na_2CO_3 is an important method of separating cations from anions (T2). (See Probs. S3 and S4, p. 744.)

Special Methods for Reducing Coprecipitation with BaSO_4

Removal of cationic interferences by ion exchange. A cation-exchange resin is a water-insoluble organic solid that adsorbs metallic ions from an aqueous solution, replacing them by an equivalent amount of H_3O^+ . The behavior of such a resin may be represented by



*If silica is present in the sample or in the Na_2CO_3 , it is taken into the basic solution and precipitates on acidification. This silica must be made insoluble by baking and must be filtered off before precipitation of BaSO_4 .

It is not the purpose of this section to describe the general properties of ion-exchange resins, but only to mention their applicability to sulfate analysis. Samuelson discusses ion-exchange processes as applied to analytical chemistry (S1).

If a solution containing sulfate and interfering metal ions is passed through a column containing a cation-exchange resin, the metal ions are quantitatively removed by adsorption onto the resin. The effluent solution contains only H_2SO_4 . (When the resin bed becomes filled with metal ions, it may be repurified by passing a concentrated acid solution through the column, reversing the foregoing equilibrium.)

Of course, H_3O^+ is still coprecipitable by BaSO_4 , but the presence of only one impurity rather than many provides a better chance of selecting conditions to give good reproducibility and accuracy. Application of this technique to analysis of sulfate solutions containing Na^+ , K^+ , Ca^{2+} , Al^{3+} , Fe^{3+} , and Cr^{3+} gives results within a few tenths of a per cent of the correct value (S1). The ion-exchange separation technique has been applied to the determination of S in ores (W12).

Homogeneous precipitation (G4). In ordinary precipitations, formation of BaSO_4 at rather high degrees of supersaturation results in imperfect crystals and contamination. Contamination is also promoted by the high local concentrations which exist where the precipitant falls into the precipitated solution. The method of homogeneous precipitation is designed specifically to avoid these high degrees of supersaturation and high local concentrations. To determine Ba^{2+} , excess sulfate precipitant is added as methyl sulfate, $(\text{CH}_3)_2\text{SO}_4$. No precipitation takes place when the precipitant is added, since methyl sulfate is not ionized and the solubility product of BaSO_4 is not exceeded. However, methyl sulfate is hydrolyzed at an elevated temperature.



This reaction is brought about slowly and homogeneously by controlling the temperature, so that SO_4^{2-} is liberated uniformly throughout the whole solution. BaSO_4 therefore forms and grows slowly and uniformly under a low degree of supersaturation. Good accuracy is claimed for the determination of Ba^{2+} in the presence of Al^{3+} , Fe^{3+} , Mg^{2+} , Na^+ , K^+ , NH_4^+ , HNO_3 , H_3PO_4 , and even Ca^{2+} . Sr^{2+} interferes. A similar procedure may be used in the determination of Pb^{2+} as PbSO_4 .

The direct determination of sulfate by homogeneous precipitation has not yet been achieved.

Empirical methods. In the determination of sulfate, coprecipitation of BaCl_2 makes results high, but coprecipitation of H_2SO_4 and alkali sulfates makes results low. It is possible to adjust conditions so that these errors compensate one another. The difficulty with such pro-

cedures is that the range of conditions over which exact compensation occurs is usually quite narrow, and conditions for performing the precipitation must be specifically stated and critically met. If the samples are fairly uniform, this technique is sometimes practical. But where the sulfate content and/or interfering substances vary at all appreciably, this technique may be ineffective (R9).

In other procedures the error is allowed to occur, but conditions are selected to make the error as reproducible as possible. The erroneous result is then corrected by a factor determined with known samples. The defects of such procedures are similar to those discussed above.

PREPARATION OF UNKNOWNNS

(See Exps. 13.1 and 13.2, pp. 214 and 221)

Chloride series. A series of 10 to 20 KCl-NaCl mixtures is recommended, each sample differing from the preceding one by about 0.15% Cl, or 0.3% relative. The samples may be made up from pure NaCl and KCl as primary standards, prepared and mixed as described on page 694. Mixtures containing sulfates are not recommended, because of the tendency of sulfate to coprecipitate. However, good results may be obtained with sulfate mixtures if the approximate chloride content of the unknown is given, so that a large excess of AgNO_3 precipitant may be avoided.

Sulfate series. A series of 10 to 20 Na_2SO_4 -NaCl mixtures is recommended, ranging from 90 to 100% Na_2SO_4 . The samples may be made up from reagent-grade Na_2SO_4 and NaCl as primary standards, prepared and mixed as described on page 694. Samples containing K salts are not recommended, because of the tendency of K to coprecipitate. If the sample contains cations other than Na, good results may sometimes be obtained by modifying the directions for analysis (F4).

SUPPLEMENTARY QUESTIONS

Section 13A

S1. On the basis of your general knowledge and the information in Table 13.1 (p. 212), outline a gravimetric method of analysis for one of the following samples. Then find the details of the method from the literature references cited on page 210. Draw a flowsheet of operations, with chemical equations for the steps involved. (a) Al in an Mg-Al alloy. (b) Cu in a Cu-Sn alloy. (c) Ni in an Fe-Cr-Ni steel. (d) Zn in a sulfide ore. (e) Na in a solution containing about 1 M NaCl and 1 M CaCl_2 .

Experiment 13.1

S1. Using chemical equations, outline procedures for analysis of the following samples, each of which contains roughly equimolar amounts of each component.

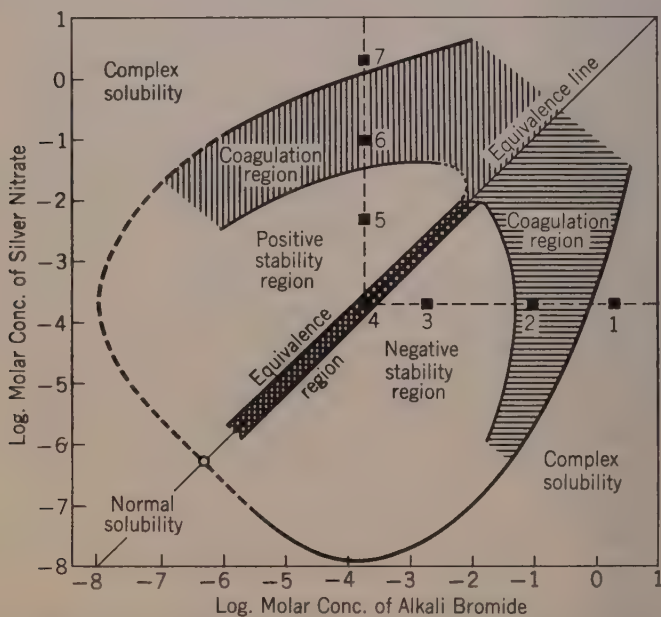
(a) AgNO_3 , KNO_3 . (b) AgNO_3 , HgNO_3 , in dilute HNO_3 . (c) KCl , KBr . (d) KCl , KI , KNO_3 . (e) KCl , KClO_3 , K_2SO_4 . (f) Dibromofluorescein ($\text{C}_{20}\text{H}_{10}\text{O}_5\text{Br}_2$), KCl . (g) KCl , KBr , KI .

S2. Outline a procedure for the gravimetric determination of chloride in sea water, assuming that it contains mostly the chlorides, with small amounts of sulfates, bromides, iodides, and borates of Na, K, and Mg.

S3. Assume that other filtering media are not available and that filter paper must be used to isolate the AgCl . Outline a procedure permitting the use of filter paper, and give equations.

S4. From the teaching standpoint, compare the relative advantages and disadvantages of each of the following chloride sample series with the one recommended on page 741. (a) Ten samples spread uniformly over the range 20–60% Cl. (b) A series of pure chlorides, such as KCl , NaCl , BaCl_2 , and NH_4Cl .

S5. Interpret the accompanying solubility diagram for the $\text{Ag}^+\text{-Br}^-$ system (M10). Describe the turbidities of the systems represented by points 1–7 on the diagram, and speculate on the mechanism of stabilization or coagulation of the system in each case.



Solubility Curve of Silver Bromide in Water at 20°C Obtained by Mixing Silver Nitrate with Alkali Bromide—Full part of the curve has been obtained experimentally using either KBr or NaBr . Both salts give solubility points on the same curve. No data are available for the dotted part of the curve which has been drawn analogously to the silver chloride solubility curve for which complete data are available. (Reprinted from E. Matijevik, J. P. Kratochvil, and M. Kerker, *Journal of Chemical Education*, 38, 397 [1961], Fig. 1, by permission of the publisher.)

Experiment 13.2

S1. In determining gravimetrically the sulfate content of a strongly basic solution, explain with equations why it is necessary to provide for separation of silica.

S2. Two different reactions are given on pages 218 and 224, to describe the reactions between chloride and nitrate in acid solution. Why are they different?

S3. If Ba were present in a sulfide ore, what would probably be its effect on the determination of total S in the ore by (a) a wet oxidation method, (b) a fusion procedure?

S4. Outline methods of analysis for the following samples, using chemical equations wherever possible. (a) An alloy containing only Ba and Pb. (b) A solution containing BaCl_2 and CaCl_2 , each at concentrations about 1 M. (c) A steel containing S. (d) A solid organic compound containing S, by a Parr bomb fusion. (e) A solution containing Na_2SO_4 and Na_2S , each at concentrations about 1 M.

S5. A sample containing CaSO_4 is to be analyzed gravimetrically for sulfate as BaSO_4 . Explain why preparation of the solution by metathesis with Na_2CO_3 might not cause severe loss of sulfate by coprecipitation with CaCO_3 . What should be done if such coprecipitation is small but appreciable?

S6. Devise a method for determining the solubility of BaSO_4 at the 1% error level. What sort of temperature control is needed?

S7. Find representative compositions of some important ores of Pb, Ni, or Zn. Outline the gravimetric determination of S in one of these ores, using chemical equations. Draw a flowsheet, showing the behavior of each constituent that may be present in an amount greater than 5%.

S8. When ion exchange is used to remove impurities from a sulfate solution, explain why the solution is passed through a column of resin, rather than just being shaken with the resin.

SUPPLEMENTARY PROBLEMS

Section 13A

S1. A 0.2000-g sample containing only KCl and NaCl gives 0.3919 g of the perchlorates. Calculate the percentage of each chloride in the mixture. In what ways could the precision of this method be improved? *Ans.* 57.7% KCl, 42.3% NaCl.

S2. What weight of sample must be taken so that each milligram of K_2PtCl_6 obtained represents two-tenths of a per cent of K in the sample?

Experiment 13.1

S1. What weight of sample should be used in order that each 0.1000 g AgCl obtained will represent 10.00% CaCl_2 in the sample? *Ans.* 0.3872 g.

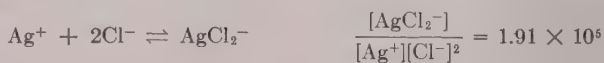
S2. In what proportions by weight should KCl and NaCl be mixed to give a sample containing 52.00% Cl?

S3. A 1.000-g sample containing only KCl and KBr gives 1.6123 g of mixed AgCl and AgBr. Calculate the % Cl in the sample. *Ans.* 4.75%.

S4. Outline a method of analysis (different from that in the example on p. 736) for a mixture containing only NaI, NaBr, and NaCl. Set up equations outlining the computations.

S5. Calculate the solubility of AgCl in solutions containing NaCl at the following concentrations: 0.0010, 0.010, 0.050, 0.10 M. Assume that only the two following

equilibria are important, and disregard activity effects. Compare results with Fig. S13.1 (p. 734).



Ans. $3.4 \times 10^{-6} M$ in $0.10 M \text{ NaCl}$.

S6. Calculate solubilities of AgCl in the NaCl solutions of Prob. S5, assuming that the formation of AgCl_2^- is negligible. Compare results with those of Prob. S5, or with Fig. S13.1.

S7. When AgCl is dissolved in pure water, show that the formation of AgCl_2^- is negligible. Use the data of Prob. S5. *Ans.* $[\text{AgCl}_2^-] = 4.5 \times 10^{-10} M$.

Experiment 13.2

S1. What weight of sample should be taken in order that each milligram of BaSO_4 obtained will represent (a) one-tenth of a per cent S in the sample, (b) one-tenth of a per cent FeS_2 in the sample? *Ans.* (a) 0.13738 g.

S2. What weight of sample should be taken so that each milligram of BaSO_4 obtained will represent one-tenth of a per cent of $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ in the sample?

S3. Suppose that a sample containing BaSO_4 is to be analyzed for sulfate, and that it is first metathesized with $2.0 M \text{ Na}_2\text{CO}_3$. (a) What is the maximum $[\text{SO}_4^{2-}]$ that may be taken into solution? (b) What is the minimum volume of $2.0 M \text{ Na}_2\text{CO}_3$ required to metathesize 0.200 g BaSO_4 ? (Hint: At equilibrium, the solution is saturated with respect to both BaSO_4 and BaCO_3 .)

$$[\text{Ba}^{2+}][\text{SO}_4^{2-}] = (K_s)_{\text{BaSO}_4}$$

$$[\text{Ba}^{2+}][\text{CO}_3^{2-}] = (K_s)_{\text{BaCO}_3}$$

Ans. (a) $0.038 M$; (b) 22 ml.

S4. Repeat the computations of Prob. S3 for the metathesis of a sample containing AgCl instead of BaSO_4 .

THE GENERAL METHOD OF VOLUMETRIC ANALYSIS

SUPPLEMENTARY PROBLEMS

Section 14A

S1. The % X in a sample is calculated from a volumetric analysis as follows:

$$\% X = \frac{100 V N E}{S}$$

V and N are the volume and normality of the standard solution, S is the sample weight, and E is the equivalent weight of X. If the relative standard deviations of sample preparation, titration, and standardizations are 0.20, 0.10, 0.10%, respectively, what is the relative standard deviation in % X? *Ans.* 0.24%.

S2. Show that it is not appreciably worth while to reduce further the error of the standardization step, if its standard deviation is less than one-third of that allowed in the titration of a sample.

S3. The relative σ of a process for preparing and measuring out a sample is 0.030, whereas that for carrying out a titration of the prepared sample is 0.010. In terms of these two relative standard deviations, compute the relative standard deviation of each result obtained in the following ways. Assume that there are no other errors in the analysis. Compare answers and draw conclusions. (a) The result obtained by using one sample and carrying out one titration on it. (b) The result obtained by using one master sample and an average titration value determined from quadruplicate titrations on aliquots of that sample. (c) Repeat part b for sixteen titrations. (d) The average result obtained by using quadruplicate samples and carrying out one titration on each. (e) Repeat part d for quadruplicate titrations on each of the four samples. (f) The average result obtained by using sixteen samples, with one titration on each. *Ans.* (a) 0.032.

Section 14B

S1. In routine titration of NaCl-KCl mixtures, what should be the sample size in order that each milliliter of 0.1300 M AgNO_3 will represent 1.000% Cl?

Ans. 0.4609 g.

S2. Devise illustrative examples for the following types of problems, to extend the selection of examples given on pages 239–42. (a) Use of selected sample weights to eliminate computations, as on page 670. (b) Indirect analysis of a mixture containing only NaCl and KCl by titration with standard AgNO_3 , as on page 671.

VOLUMETRIC APPARATUS AND TECHNIQUES

SPECIFICATIONS AND TOLERANCES FOR VOLUMETRIC EQUIPMENT

(See Sec. 15A, p. 245)

When a liquid that wets glass is delivered from a buret or pipet, some of the liquid is retained on the inner wall. Unless delivery is extremely slow, the volume held back will be greater than that required to form a wetting film, and the excess liquid will drain down slowly. Therefore

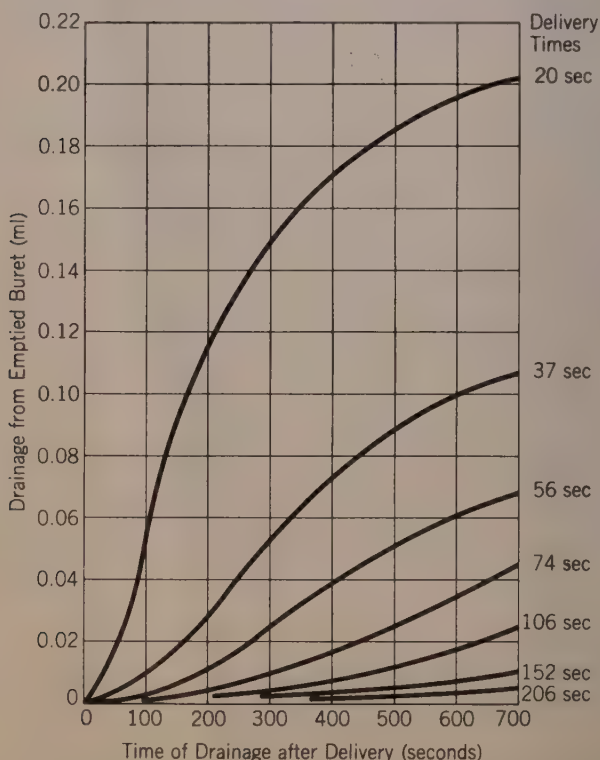


FIG. S15.1. Drainage from a 50-ml Buret for Various Delivery and Drainage Times (Reprinted from V. Stott, *Journal of the Society of Glass Technology*, 5, 307 [1921], Fig. 2, by permission of the publisher.)

the volume of a given liquid delivered by a piece of apparatus depends upon the position during delivery and the time allowed for drainage. Figure S15.1 shows the volume after drainage from an ordinary 50-ml buret as a function of time after delivery, for various delivery times (S29). Pipets show similar behavior (Fig. S15.2).

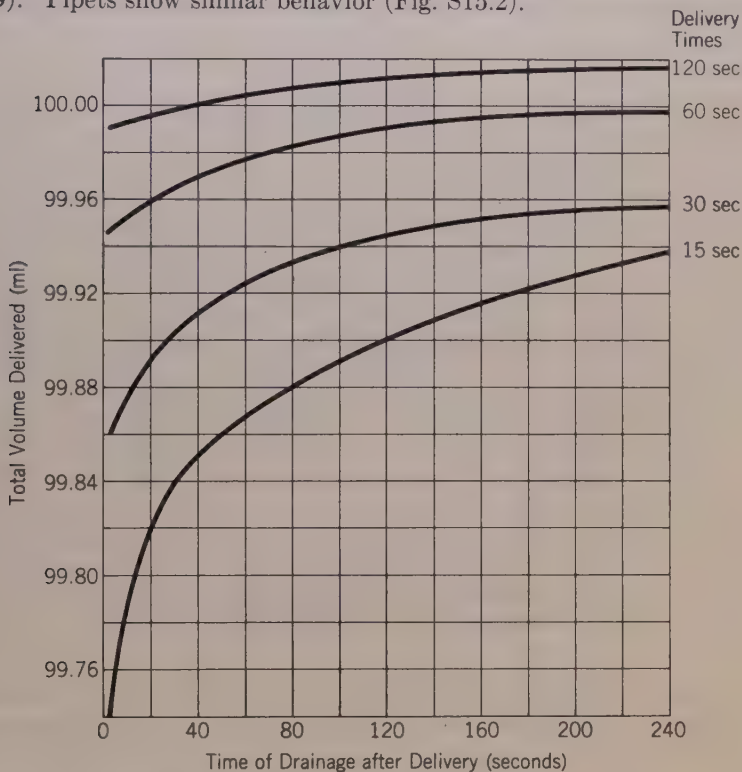


FIG. S15.2. Volumes Delivered from a 100-ml Pipet for Various Delivery and Drainage Times (Reprinted from V. Stott, *Journal of the Society of Glass Technology*, 7, 169 [1923], Fig. 5, by permission of the publisher.)

Examination of Figs. S15.1 and S15.2 shows that unless delivery time is fairly long, the volume delivered is critically dependent upon the time allowed for drainage. For accurate work, therefore, the tip of a buret or a pipet is constricted; as a result, the delivery time is sufficiently long to ensure that reasonable variations in drainage time do not cause great errors in the volume delivered. This precaution is more important for a buret than for a pipet, since drainage time for the pipet can usually be controlled, whereas the time required to carry out a titration with a buret may vary uncontrollably. The National Bureau of Standards

recommends certain dimensions and delivery times for burets and pipets, dependent upon capacity (U6).

In addition, the National Bureau of Standards recommends that the nominal capacity of any piece of volumetric equipment be accurate within the limits shown in Table S15.1. Manufacturers in the United

TABLE S15.1
TOLERANCES FOR BURETS, PIPETS, AND FLASKS *

CAPACITY (ML) LESS THAN AND INCLUDING	TOLERANCE AT MAXIMUM CAPACITY (ML)		
	Burets	Pipets (Transfer)	Flasks (To Contain)
2.....		0.006	
5.....	0.01	0.01	
10.....	0.02	0.02	
25.....			0.03
30.....	0.03	0.03	
50.....	0.05	0.05	0.05
100.....	0.10	0.08	0.08
200.....		0.10	0.10
300.....			0.12
500.....			0.15
1000.....			0.30
2000.....			0.50
5000.....			1.2

*Data taken in part from J. C. Hughes, "Testing of Glass Volumetric Apparatus," National Bureau of Standards Circular 602, April, 1959, Tables 9, 10, and 11, with permission of the publisher.

States meet these specifications with their better grades of volumetric equipment. For a reasonable fee the Bureau will calibrate apparatus that meets these specifications.

MISCELLANEOUS VOLUMETRIC TECHNIQUES

(See Sec. 15B, p. 248)

Measurement of odd volumes. It is occasionally necessary to measure out accurately an odd volume of solution not in the range of common volumetric equipment. The procedures for doing this are varied, and depend on the ingenuity of the worker. A desired volume may always be obtained very accurately by weighing, if the density is known; if the density is not known, it may always be found by weighing any accurately measured and convenient volume. A volume close to that obtainable by an available piece of equipment may be obtained by adding or subtracting with a buret or measuring pipet. Of course, any volume corresponding to the sum (or difference) of volumes obtain-

able with available equipment may be measured out, but the accumulation of error makes this method less desirable as the number of component volumes increases.

Preparation of a solution of a particular concentration. For some applications a standard solution of a certain concentration must be accurately prepared. If the solute is a primary standard, the amount of substance required may be accurately weighed out and diluted to volume in a volumetric flask. (The buoyancy correction for this weighing may sometimes be appreciable.) If the solute is not a primary standard, a solution is prepared that has a concentration slightly higher than that desired. The resulting solution is standardized, and the extent to which it must be diluted may be calculated from the difference between the observed and desired concentrations. The dilution is carried out, and the resulting solution is standardized and diluted again if necessary. With experience, one dilution often suffices, and more than two are seldom necessary.

Marking volumetric equipment. Sometimes calibration marks must be made upon flasks and pipets in addition to ones already there. Such marks may be made in two ways. The edge of a gummed label may be placed at the position to be marked, and the calibration data may be conveniently written on the label. After being lacquered, the label is semipermanent; it resists many washings, but is removed or destroyed by prolonged soaking or treatment with concentrated acids or alkalies. A more permanent mark may be made by etching the glass as follows: The position of the mark is located with a strip of gummed paper completely encircling the flask. Then the label and the flask are coated with beeswax for several centimeters above and below the mark. The flask is loosely clamped above the mark, with the neck in a horizontal position, and the body resting on the table top. Next, a line is cut through the beeswax with the blade of an old knife held against the neck of the flask with one hand, while the other hand rotates the flask slowly. Then, while the flask is still rotating, a few drops of conc. HF are placed on the cut. Etching is sufficient when the surface under the knife blade feels rough (U6).

Use and preservation of standard solutions. Standard solutions are not indefinitely stable. The following techniques are commonly used to prevent changes in concentration. (1) All standard solutions must be kept in closed containers to prevent evaporation. (2) All containers should be shaken before use, to prevent nonuniformity in concentration caused by condensation of solvent on the upper parts of the container. This is particularly important when the volume of solution is small compared to the volume of the bottle. (3) To remove dirt or encrusted solute, the lip of the bottle should be wiped with a damp cloth before the

stopper is removed. After the solution is withdrawn, any droplets adhering to the top of the bottle should be carefully wiped away before the stopper is reinserted. (4) Some solutions react with air, and must be stored and used out of contact with air. Thus standard base is often stored and used in the manner shown in Fig. 18.7 (p. 360), to prevent absorption of CO_2 from the air. Strongly reducing solutions must be stored and used out of contact with oxygen from the air. (5) Some solutions react with glass and must be stored in special kinds of containers. Standard base is best stored in plastic bottles, or in paraffin-lined glass bottles. (6) Some standard solutions are unstable with respect to special reactions. AgNO_3 and KMnO_4 solutions are slowly decomposed by light, and should be stored in the dark or in brown bottles. $\text{Na}_2\text{S}_2\text{O}_3$ is subject to bacterially induced decomposition, and should be stored with a preservative.



FIG. S15.3. Morse-Blalock Bulb for Calibrating Volumetric Flasks

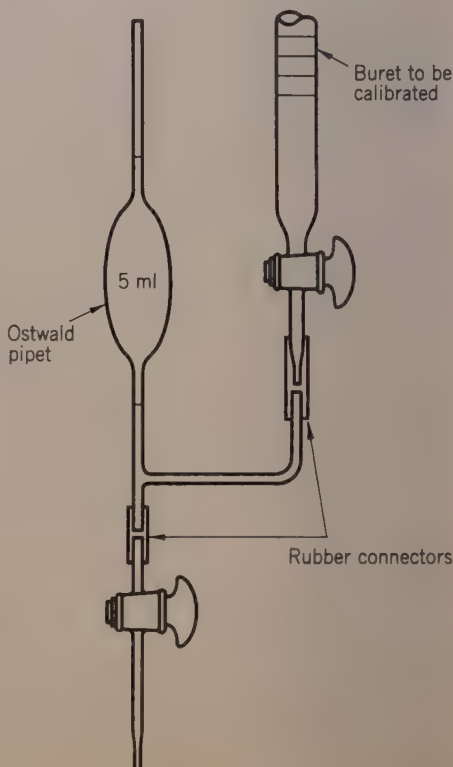


FIG. S15.4. Ostwald Pipet for Calibrating Burets

OTHER METHODS OF CALIBRATION

(See Sec. 15C.2a, p. 263)

Volumetric equipment may also be calibrated by comparing its volume with that of a standard piece of equipment. For example, flasks may be conveniently calibrated with Morse-Blalock calibration bulbs (Fig. S15.3). The neck of the calibration bulb should be small compared to the neck of the flask; then the error of reading the volume of the bulb is small compared to the error of reading the flask to be calibrated. Burets may be calibrated with pipets of the Ostwald type, the operation of which may be deduced from Fig. S15.4. Although the Ostwald method is rapid, drainage conditions do not resemble those which apply in an ordinary titration; neither, therefore, do the calibration corrections. The principal advantage of volumetric methods of calibration is their speed, especially when many pieces must be calibrated. The disadvantage is that special equipment is required. Although adequate for most purposes, volumetric methods of calibration are less accurate than gravimetric ones.

For calibrating micropipets, Hg is used because of its high density. Since it does not wet glass, the volume of Hg delivered is the same as the volume contained.

COMPUTATION OF THE VOLUME OF A GLASS VESSEL FROM THE WEIGHT OF WATER CONTAINED (U6)

(See Sec. 15C.2a, p. 263)

To show how the specific volumes in Table 15.1 (p. 264) are derived, one of these volumes is calculated in the following example.

Example. What is the volume at 20°C of a flask that contains one gram of water at 30°C, weighed in air against brass weights?

The density of water at 30°C is 0.99564 g/ml (L4). This is expressed as a weight in vacuum per milliliter, and before this density may be used to compute the volume of the one gram in air, the air weight must be converted to a weight in vacuum. Taking the density of air at 30°C as 1.16 mg/ml, the weight in vacuum of one gram in air is

$$1.00000 + (1.00000)(0.00116) \left[\frac{1.00}{1.00} - \frac{1.00}{8.0} \right] = 1.00101 \text{ g}$$

The volume of water (and therefore of the flask) at 30°C is therefore $1.00101/0.99564 = 1.00539$ ml.

At 20°C, the volume of the flask is somewhat less than at 30°C, since the glass contracts as temperature decreases. The expansion coefficient of glass is only 0.0025%/°C, or 0.025%/10°C. The volume of the flask at 20°C is therefore less than the volume at 30°C by $(0.00025)(1.00539) = 0.00025$ ml.

Hence the volume of the flask at 20°C is $1.00539 - 0.00025 = 1.0051$ ml, as in Table 15.1.

SUPPLEMENTARY QUESTIONS

Section 15A

S1. Cite the relative advantages and disadvantages of using a buret with a delivery time of 20 seconds as compared to one of 74 seconds.

S2. A 50-ml buret has a delivery time of 74 seconds. If a titration procedure requires anywhere from 1 to 3 minutes, specify the most convenient range of time over which the final readings may be taken in order that the error due to variable drainage will be less than 0.01 ml. Specify the range for a titration that may take anywhere from 1 to 10 minutes.

S3. Repeat Ques. S2 for a buret with a delivery time of only 20 seconds, and compare the answers.

S4. Considering the mechanism responsible for drainage, explain why the curves of Fig. S15.1 (p. 746) are **S**-shaped.

S5. Several hundred 25-ml portions of a certain stable standard solution are to be metered out every day, with a standard error of around 0.1%. Design and describe apparatus which might be used to perform this metering with a minimum of effort.

S6. From Fig. S15.2 (p. 747), give the volumes delivered for the two following cases. (a) 30-second delivery plus 120-second drainage. (b) 120-second delivery plus 30-second drainage. The total times are the same, but the volumes are different. Explain.

S7. The National Bureau of Standards has specified tolerances on flasks to deliver. How would these compare with the tolerances in Table S15.1 (p. 748)?

Section 15C

S1. In calibrating a good buret with an Ostwald pipet, it is found that the calibration correction is always positive and increases quite uniformly with increase in volume. Explain.

S2. Devise a method of calibrating a small pipet with mercury. How would this pipet have to be used to measure out aliquots of aqueous solutions?

S3. What errors associated with the ordinary buret are avoided in using the weight buret?

S4. Densities of water are known very accurately, with uncertainties of the order of only a few p.p.m. How accurately would the buoyancy corrections, densities of air and brass, and the expansion coefficient of glass have to be known in order to compute the volumes of Table 15.1 (p. 264) to six significant figures? Explain the associated measurements (i.e., of temperature, atmospheric pressure, etc.) which would have to be made to achieve this precision.

S5. Suppose that a solution is measured as 0.10000 *N* at 20.0°C, and that it is desired to compute its concentration at 30.0°C. There is an interesting and basic philosophical question here, as to whether only the expansion of the solution need be considered, or whether the differential expansion between the solution and glass should be used in the computation, as is done in Table 15.1. Discuss this dilemma (**B25**).

S6. Design a piece of volumetric equipment which may be used to deliver any volume between 200 and 250 ml of an aqueous solution, measurable with an error of about 0.05 ml or less.

S7. Outline the steps by which a 50-ml pipet may be calibrated and marked so that it delivers precisely 50.00 ml.

S8. The standard deviation of measurements made with ordinary volumetric

equipment is around 0.01 ml. Bishop (B12) has described techniques and precautions that can be used to bring the standard deviation down to 0.001 ml. Summarize Bishop's paper.

SUPPLEMENTARY PROBLEMS

Section 15C

S1. What difference might be expected in the two following ways of calibrating a buret with a 37-second delivery time for 50-ml delivery? (a) The ordinary way, with about 3 minutes between initial and final readings. (b) With a 5-ml Ostwald pipet, a process which requires 15 minutes.

Ans. Volume delivered is about 0.11 ml greater with the Ostwald pipet.

S2. The σ of reading the position of the meniscus is 0.2 mm, both for a volumetric flask to be calibrated, and for a Morse-Blalock calibrating bulb. What must be the ratio of the neck diameters of the bulb and flask in order for the σ of reading the volume of the bulb to be less than one-third that of reading the volume of the flask?

S3. Derive the volume per gram of water at 35°C that is given in Table 15.1 (p. 264).

S4. From the data of Table 15.1, compute the average differential expansion coefficient of water in glass between 20° and 30°C. What is the coefficient between 15° and 20°C? Between 30° and 35°C? Discuss the adequacy of 0.02% per °C for the range 15–35°C.

S5. At 27°C, a 0.1-ml micropipet delivers 1.3537 g of mercury, weighed in air against brass weights. What is the volume of the pipet at 20°C? (The density *in vacuo* of mercury at 27°C is 13.5290 g/ml (L4).)

Ans. 0.1006 ml.

TITRATIONS BASED ON PRECIPITATION REACTIONS

ERROR OF TITRATING TO THE INFLECTION POINT IN PRECIPITATION TITRATIONS

(See Sec. 16B, p. 279)

Titration to the inflection point (i.e., the point on the titration curve corresponding to the steepest slope) is frequently used to establish the equivalence point. The experimental procedure is outlined for acid-base titrations on page 351. For symmetrical titration curves (e.g., $\text{Ag}^+\text{-Cl}^-$, $\text{Ba}^{2+}\text{-SO}_4^{2-}$, etc.), there is no determinate error in this procedure, since the inflection point coincides with the equivalence point. However, for unsymmetrical titration curves (e.g., $\text{Ag}^+\text{-CrO}_4^{2-}$), the inflection point does not coincide with the equivalence point, and there is a determinate titration error. In this section, the magnitude of the titration error is calculated for a precipitation titration of the Ag_2CrO_4 type.

Suppose that a solution containing A mmoles of AgNO_3 is titrated with C M K_2CrO_4 , and that the volume of the system is practically constant at V ml in the region of the equivalence point.

In outline, the problem may be solved by first finding the equation of the titration curve (i.e., $p\text{Ag}$ vs. ml of K_2CrO_4), and then setting the second derivative of this curve equal to zero to find the composition of the titrated solution at the inflection point, after which the end-point error may be calculated.

Bolie (B19) gives a single equation for the whole titration curve, but the differentiation of this equation is exceedingly difficult. A preliminary survey of the problem reveals simplifications that make the solution easier.

The solubility-product equilibrium that defines the titration curve is



Because of the squared dependence on $[\text{Ag}^+]$, it is readily apparent that the titration curve will be steeper before the equivalence point (where excess Ag^+ is being diminished) than after (where excess CrO_4^{2-} is being built up). The point of steepest slope will therefore come at or before

the equivalence point, and only this region of the titration curve need be considered.

Secondly, a proper choice of the independent variable lightens the problem. Since the inflection point falls close to the equivalence point, it is best to let the independent variable be

$$x = [\text{Ag}^+] - 2[\text{CrO}_4^-] \quad (Sb)$$

Here, x represents the excess concentration of Ag^+ over that of CrO_4^- . The titration error is proportional to x , which is positive before the equivalence point, and zero at the equivalence point.

Combination of Eqs. *Sa* and *Sb* gives the equation for the titration curve.

$$[\text{Ag}^+]^2 \left(\frac{[\text{Ag}^+] - x}{2} \right) = K_s \quad (Sc)$$

For convenience in symbolism, omit the brackets and charge on $[\text{Ag}^+]$. Eq. *Sc* may be put into logarithmic form and differentiated to find the slope of the titration curve.

$$\frac{d(p\text{Ag})}{dx} = \frac{d(\text{Ag})/dx - 1}{2(\text{Ag} - x)} \quad (Sd)$$

The second derivative may be found and set equal to zero to find the inflection point.

$$\frac{d^2(p\text{Ag})}{dx^2} = \frac{(\text{Ag} - x)(d^2(\text{Ag})/dx^2) - (d(\text{Ag})/dx - 1)^2}{(\text{Ag} - x)^2} \quad (Se)$$

$$(\text{Ag} - x)(d^2(\text{Ag})/dx^2) = (d(\text{Ag})/dx - 1)^2 \quad (\text{At the inflection point}) \quad (Sf)$$

Before Ag at the inflection point may be defined by Eq. *Sf*, the first and second derivatives of Ag with respect to x must be found by differentiating Eq. *Sc*.

$$\frac{d(\text{Ag})}{dx} = \frac{\text{Ag}}{3\text{Ag} - 2x} \quad (Sg)$$

$$\frac{d^2(\text{Ag})}{dx^2} = \frac{6\text{Ag}(\text{Ag} - x)}{(3\text{Ag} - 2x)^3} \quad (Sh)$$

Eqs. *Sf*–*Sh* may be combined to eliminate the derivatives.

$$\text{Ag} = 4x/3 \quad (\text{At the inflection point}) \quad (Si)$$

Eqs. *Sc* and *Si* may finally be combined to define x at the inflection point.

$$x_{\text{infl}} = \frac{3}{2} \sqrt[3]{K_s} \quad (Sj)$$

For Ag_2CrO_4 , $K_s = 1.29 \times 10^{-12}$, and x_{infl} is $1.7 \times 10^{-4} M$. The inflection point comes when the excess of Ag^+ over $\text{CrO}_4^{=}$ is 1.7×10^{-4} moles per liter. If the equivalence-point volume is V ml, the excess Ag^+ is $1.7 \times 10^{-4} V$ mmoles. The volume of $C M$ K_2CrO_4 equivalent to this excess of Ag^+ is $1.7 \times 10^{-4} V/2C$, which represents the titration error in terms of ml of standard K_2CrO_4 .

For a typical titration, V might be 100 ml, and C might be 0.0500 M K_2CrO_4 , giving a titration error of 0.17 ml, which is substantial.

ADSORPTION INDICATORS

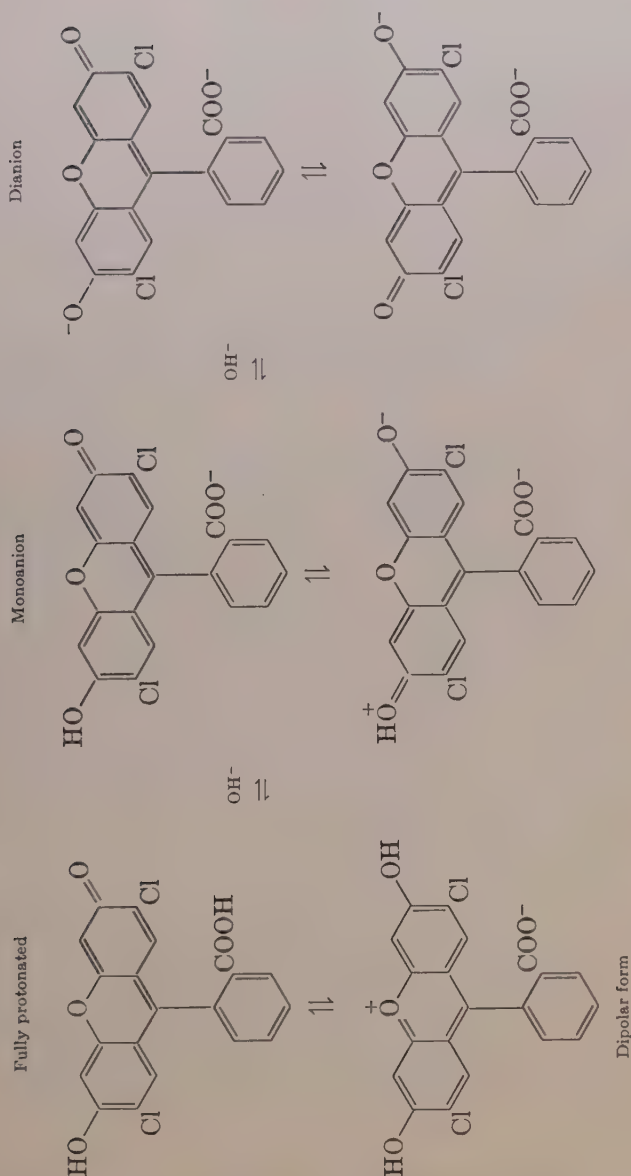
(See Sec. 16B.5, p. 286, and Exp. 16.2, p. 295)

Dichlorofluorescein is related in structure to phenolphthalein, which is an acid-base indicator and a triphenylmethane dye (**c8**). Indicators are organic substances with fairly complicated structures, having chromophoric groups ($>\text{C}=\text{C}<$, $>\text{C}=\text{O}$, $-\text{N}=\text{N}-$, $-\text{NO}_2$) as well as auxochromic groups ($-\text{OH}$, $-\text{NH}_2$). It is the electrons in the chromophoric groups that become energized upon absorption of visible light, and whose configuration determines the wave length and intensity of absorption. The auxochromic groups may modify the absorption greatly.

If there is a high degree of conjugation, the molecules can be excited rather easily to higher electronic states by visible light quanta (380–770 $m\mu$), and the compounds are highly colored. In most cases, the absorbed light energy is dissipated as heat, but in some cases it may be reemitted (fluorescence), or in other cases it may initiate photochemical reactions involving the absorbing molecules.

In order to possess indicator properties, the molecule must be able to undergo electronic rearrangement without extensive or irreversible changes in chemical bonding. Acid-base and redox indicators are discussed in other parts of this text, while the behavior of dichlorofluorescein is summarized in the structural equations on page 757.

Dichlorofluorescein is a weak acid ($pK_a = 4$) that may exist in tautomeric forms. (Tautomers are isomeric forms of a substance that exist in rapid reversible equilibrium with each other, and that differ only in location of a proton.) The dianionic form possesses considerable conjugation, and, in addition, can resonate between the two forms shown. It is yellow with an intense green fluorescence. The absorption maximum falls at 500–510 $m\mu$. The acid form shows no fluorescence. When Ag^+ coordinates with the ions, either in a precipitate or in an adsorbed-ion layer, still another structure must be stabilized, because an intense red



color not possessed by the uncoordinated forms appears. The nature of the complex with Ag^+ is not given in the literature.

A particular indicator is not suitable for all titrations, but a sufficient variety of indicators is available to permit choice of a suitable indicator. Thus, eosin is not suitable for the titration of Cl^- with Ag^+ , because

eosinate is adsorbed too strongly compared to Cl^- , and the end point comes too soon. On the other hand, eosin works well for Br^- , SCN^- , and I^- , since each is more strongly adsorbed than eosinate by the silver salt. For the Ag^+ - Cl^- titration, less adsorbable indicators like fluorescein or dichlorofluorescein must be used.

TABLE S16.1
SOME TITRATIONS WITH ADSORPTION INDICATORS*

Indicator	Titrated Ion	Titrant	pH	Color Change
Fluorescein	Cl^- , Br^- , I^- , SCN^- , CN^- , OCN^- , $\text{Fe}(\text{CN})_6^{4-}$	Ag^+	7-8	yellow to red
	$\text{C}_2\text{O}_4^{2-}$, CO_3^{2-} , OH^- , SO_4^{2-}	Pb^{2+} Ba^{2+}	neutral basic	yellow to red yellow to red
Dichloro- fluorescein	Cl^- , Br^- , I^- , SCN^- , $\text{Fe}(\text{CN})_6^{4-}$	Ag^+	4-8	yellow to red
	Mercaptobenzthi- azole PO_4^{3-} , BO_2^- , OH^-	Ag^+ Pb^{2+}	alc. NH_3 neutral	yellow to red yellow to red
Eosin	Br^- , I^- , SCN^-	Ag^+	2-8	pink to red
	MoO_4^{2-} † SO_4^{2-}	Pb^{2+} Pb^{2+}	.01 M HAc neutral	pink to red pink to red
Bromphenol blue	Cl^- , Br^-	Hg_2^{2+}	dilute acid	yellow to lilac
	Ag^+	I^-	5-7	green to purple
	I^- †	Tl^+	4-8	yellow to green
	Cl^- , I^- , SCN^-	Ag^+	3-8	purple to green
Rhodamine 6G	Ag^+	Br^- , Cl^-	0.3 M HNO_3	orange to violet

*The following titrations have also been reported: F^- with Ca^{2+} or Ce^{4+} ; SeO_3^{2-} with Ag^+ ; CrO_4^{2-} , WO_4^{2-} , and $\text{Fe}(\text{CN})_6^{3-}$ with Pb^{2+} ; $\text{Fe}(\text{CN})_6^{4-}$ with Ag^+ , Zn^{2+} , or Pb^{2+} ; Zn^{2+} with $\text{Fe}(\text{CN})_6^{3-}$; Pb^{2+} with CO_3^{2-} , SO_4^{2-} , CrO_4^{2-} , or MoO_4^{2-} ; Hg^{2+} with $\text{C}_2\text{O}_4^{2-}$.

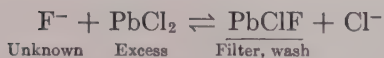
†Reverse titrations are also performable.

Table S16.1 lists some adsorption indicators (J3, W5). It should be noted that there are weak base adsorption indicators (like rhodamine 6G) that are adsorbed as cations to give the color change; these permit the direct titration of Ag^+ with standard sodium halide, which cannot be done with dichlorofluorescein. Some acid-base indicators (like bromphenol blue) can also function as adsorption indicators. Some adsorption indicators are adsorbed throughout the whole titration, but undergo a color change at the equivalence point.

OTHER ARGENTIMETRIC TITRATIONS

(See Sec. 16C, p. 289)

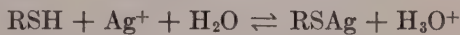
Determination of fluoride as PbClF . The mixed compound PbClF is only moderately insoluble, but its solubility may be decreased by an excess of PbCl_2 .



The PbClF is dissolved in acid, and the chloride is determined by the Volhard method. This method is not strictly stoichiometrical; the composition of PbClF varies slightly unless the fluoride and chloride concentrations are kept within certain limits.

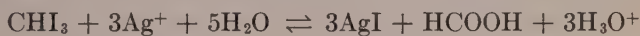
Determination of organic compounds (K19). Organic compounds react in a variety of ways with Ag^+ , and some compounds may be determined argentimetrically on the basis of these reactions. Representative examples follow. The relative errors associated with most of these methods are of the order of 1%.

1. Mercaptans (and related compounds, such as xanthates) form insoluble Ag salts.

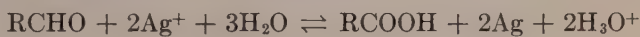


Excess standard AgNO_3 is added to an alcoholic solution of the mercaptan. After reaction, the excess Ag^+ is determined by the Volhard method without removing the precipitate of RSAg .

2. Iodoform (and other hydrolyzable compounds containing halogen) may be determined by adding excess standard AgNO_3 to an acidified alcoholic solution. Considerable time is required for complete reaction, after which the excess Ag^+ is determined by the Volhard method.

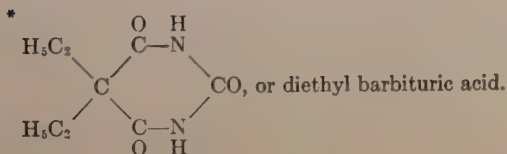
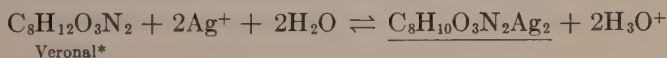


3. Aldehydes are oxidized to the corresponding organic acids by Ag^+ , which in turn is reduced to metallic silver.



Excess standard AgNO_3 is added to an alkaline solution, and time is allowed for complete reaction. After reaction, the mixture is acidified, filtered, and the excess Ag^+ in the filtrate is determined volumetrically.

4. Barbituric acid and its derivatives form insoluble Ag salts.



This reaction is the basis of a direct titration with standard AgNO_3 , K_2CrO_4 being used as an indicator. The titrated solution must be buffered (with sodium borate) so that the acid produced by the reaction does not build up as titration proceeds, since this would prevent complete reaction and would also interfere with the action of the chromate indicator.

TITRATION OF MIXTURES

(See Sec. 16C, p. 289)

If a sample contains two components (such as NaI and NaCl) that form insoluble products with the same standard reagent (AgNO_3), and if the products (AgI and AgCl) are of considerably different solubilities, then it is theoretically possible to titrate each component individually in the mixture, and to obtain two end points. Since AgI is much more insoluble than AgCl , $[\text{Ag}^+]$ is kept so low that the solubility product of AgCl is not exceeded in that part of the titration where excess iodide is present. Only when practically all iodide is precipitated and $[\text{I}^-]$ becomes very low may $[\text{Ag}^+]$ rise sufficiently to exceed the solubility product of AgCl , which then begins to precipitate. The first sharp rise of $[\text{Ag}^+]$ corresponds to the equivalence point for iodide. After all iodide

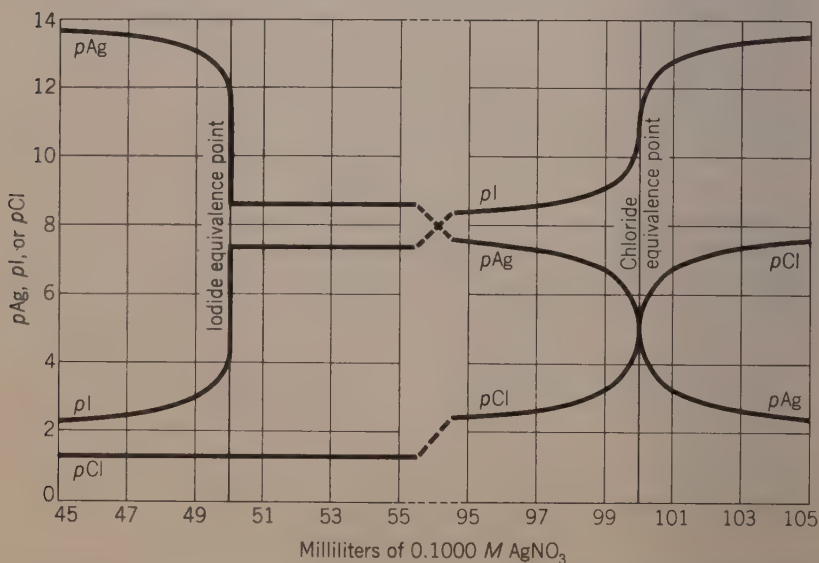


FIG. S16.1. Titration Curves for a Mixture of NaI and NaCl —Conditions: 50.00 ml of 0.1000 M NaI and 0.1000 M NaCl titrated with 0.1000 M AgNO_3 . K_s for AgCl is 1.00×10^{-10} ; K_s for AgI is 1.00×10^{-16} .

is precipitated, and more AgNO_3 is added, AgCl precipitates until $[\text{Cl}^-]$ becomes very low, at which point $[\text{Ag}^+]$ undergoes a second sharp rise, corresponding to the equivalence point for chloride.

Curves for the titration of a mixture of NaI and NaCl with standard AgNO_3 are shown in Fig. S16.1. The mode of computing points on the curves is shown in the following illustrative examples. In the calculations it is assumed for simplicity that (1) volumes are additive, (2) activity and complexation effects are nil, and (3) solubility products are 1.00×10^{-10} for AgCl and 1.00×10^{-16} for AgI . The curves are therefore approximate ones, designed only to show how the ion concentrations change in the course of the titration.

Example S1. A 50.00-ml portion of a solution containing 0.1000 M NaI and 0.1000 M NaCl is titrated with 0.1000 M AgNO_3 . Using the assumptions of the preceding paragraph, calculate $p\text{I}$, $p\text{Cl}$, and $p\text{Ag}$ when 49.00 ml AgNO_3 are added.

Since AgI is so much more insoluble than AgCl , assume that the added AgNO_3 is quantitatively precipitated as AgI , and that no AgCl is precipitated. This precipitation leaves an excess of 1.00 ml of 0.1000 M NaI and 50.00 ml of 0.1000 M NaCl in a volume of 99.00 ml. Hence

$$\text{Excess NaCl} = \frac{0.1000 \times 50.00}{99.00} = 0.0505 M$$

and
$$[\text{Cl}^-] = 0.0505 M$$

Therefore
$$p\text{Cl} = -\log [\text{Cl}^-] = -\log (0.0505) = 1.30$$

$$\text{Excess NaI} = \frac{0.1000 \times 1.00}{99.00} = 0.00101 M$$

The highly insoluble AgI probably does not contribute appreciably to $[\text{I}^-]$, which may therefore be assumed to come exclusively from the excess NaI . Therefore

$$[\text{I}^-] = 0.00101 M \quad \text{and} \quad p\text{I} = 3.00$$

$[\text{Ag}^+]$ may be calculated from the solubility product of AgI .

$$[\text{Ag}^+] = \frac{1.00 \times 10^{-16}}{[\text{I}^-]} = \frac{1.00 \times 10^{-16}}{0.00101} = 9.9 \times 10^{-14} M$$

$$p\text{Ag} = -\log (9.9 \times 10^{-14}) = 13.00$$

Note that since the solubility of AgI is only about $10^{-13} M$, its contribution to $[\text{I}^-]$ is negligible, and the second of the assumptions above is justified. All points up to the iodide equivalence point may be calculated in this way, except those that are extremely close to the equivalence point.

Note also that $[\text{Ag}^+][\text{Cl}^-] = (10^{-13})(0.0505) = 5 \times 10^{-15}$, which is less than K_s for AgCl . Hence no AgCl precipitates, which justifies the first of the above assumptions.

Example S2. For the titration of Ex. S1, calculate the ion concentrations when 50.00 ml of AgNO_3 are added, and when AgCl just begins to precipitate.

Since AgI is so much more insoluble than AgCl , assume that the added AgNO_3

is quantitatively precipitated as AgI. Since no appreciable amount of AgCl is yet precipitated, there is an excess of 50.00 ml of 0.1000 *M* NaCl in a volume of 100.00 ml, and the excess NaCl concentration is $0.1000 \times 50.00/100.00 = 0.0500$ *M*. Hence $[\text{Cl}^-] = 0.0500$ *M*, and $p\text{Cl} = 1.30$.

Since AgCl is about to precipitate, the solubility-product expression for AgCl holds, and

$$[\text{Ag}^+] = \frac{1.00 \times 10^{-10}}{[\text{Cl}^-]} = \frac{1.00 \times 10^{-10}}{0.0500} = 2.00 \times 10^{-9} \text{ } M$$

$$p\text{Ag} = 8.70$$

$[\text{I}^-]$ may be calculated from K_s for AgI.

$$[\text{I}^-] = \frac{1.00 \times 10^{-16}}{[\text{Ag}^+]} = \frac{1.00 \times 10^{-16}}{2.00 \times 10^{-9}} = 5.00 \times 10^{-8} \text{ } M$$

$$p\text{I} = 7.30$$

In the light of the answers obtained, the two assumptions may be justified as in Ex. S1.

This point corresponds to the iodide equivalence point, which comes at the first "break" in the titration curve. While the titration curve for iodide alone would be smooth and S-shaped in the region of the equivalence point, the onset of AgCl precipitation causes a break, or discontinuity, as shown in Fig. S16.1.

Example S3. For the titration of Ex. S1, calculate the ion concentrations when 51.00 ml AgNO₃ are added.

Since AgI is so much more insoluble than AgCl, assume that all iodide is precipitated as AgI, using up 50.00 ml of the AgNO₃. Assume that the remaining 1.00 ml AgNO₃ is precipitated as AgCl, leaving an excess of 49.00 ml of 0.1000 *M* NaCl in a volume of 101.00 ml. The excess NaCl concentration is therefore $0.1000 \times 49.00/101.00 = 0.0485$ *M*. If it is assumed that $[\text{Cl}^-]$ is contributed to principally by the excess NaCl, and not appreciably by AgCl, $[\text{Cl}^-] = 0.0485$ *M*, and $p\text{Cl} = 1.31$.

Since the solution is saturated with both AgCl and AgI, $[\text{Ag}^+]$ and $[\text{I}^-]$ may be calculated as in Ex. S2.

$$[\text{Ag}^+] = \frac{1.00 \times 10^{-10}}{[\text{Cl}^-]} = \frac{1.00 \times 10^{-10}}{0.0485} = 2.06 \times 10^{-9} \text{ } M$$

$$[\text{I}^-] = \frac{1.00 \times 10^{-16}}{[\text{Ag}^+]} = \frac{1.00 \times 10^{-16}}{2.06 \times 10^{-9}} = 4.85 \times 10^{-8} \text{ } M$$

$$p\text{Ag} = 8.69$$

$$p\text{I} = 7.31$$

Note that the contribution of AgCl toward $[\text{Cl}^-]$ is only 2×10^{-9} *M*; this figure is negligible compared to 0.0485 *M* and justifies the foregoing assumptions. These assumptions may be applied to within about 0.1 ml of the chloride equivalence point. Closer, the solubility of AgCl becomes appreciable compared to the excess NaCl concentration, and a quadratic equation must be solved.

To give a satisfactory indication of the iodide equivalence point, an indicator is required that will transit at $p\text{Ag} = 9 - 12$. It is possible

to establish this equivalence point with any of several adsorption indicators, dimethyldiiodofluorescein being among the best. This indicator is adsorbed by AgI more strongly than is chloride, and gives a fairly satisfactory end point for iodide in the presence of chloride. The sum of iodide plus chloride may be found by titrating another aliquot of sample using fluorescein as an indicator. In titrations that have a double end point, it is usually more satisfactory to obtain the end point potentiometrically.

In general, the accuracy of precipitation titrations with double end points is not high. Even though the solubility product of the more soluble compound is theoretically not exceeded until the first equivalence point is reached, other conditions favor the coprecipitation of the more soluble precipitate with the less soluble one. In particular, Ag halides form mixed crystals or solid solutions, and errors in the titration of mixtures of halides with standard AgNO_3 are of the order of several per cent (L2). In particular, coprecipitation of a more soluble halide (like AgCl or AgBr) on AgI causes a rounding at the sharp break of the curve in Fig. S16.1. An S-shaped curve results, but the point of steepest inflection falls past the equivalence point. Results are high for the less soluble component (iodide), and correspondingly low for the more soluble one (chloride or bromide). Corrections are difficult to apply, because the extent of coprecipitation is variable, depending on such difficultly controllable factors as the rate of titration and the ratio of the concentrations of the host and coprecipitated substances.

PREPARATION OF STUDENT SAMPLES

(See Sec. 16D, p. 291)

For chloride unknowns, the NaCl-KCl mixtures described on page 741 are appropriate. Mixtures containing sulfate are not recommended.

It is expedient to use powdered samples for the Ag-Cu alloy of Exp. 16.3. An appropriate series has ten to twenty members, in a range from 50 to 60% Ag, consecutive individual members differing from one another by about 0.15% Ag, or 0.3%, relative. The series may be prepared by mixing carefully weighed portions of two master samples, one containing about 50% Ag and the other about 60% Ag, as described on page 694. Only the compositions of the two master samples need be established by analysis, and the compositions of the intermediate samples may be calculated. Powdered samples (100 mesh or finer) of silver solder (Ag-Cu-Zn) are available from manufacturers of powdered metals.

Sheets of bullion metal or of some silver solders are very uniform and serve well for unknown samples. It is possible to cut these sheets into the proper sample size before they are issued to students. The difficulty

with sheets is that each sample requires individual analysis in order to establish the correct composition. Also, sheets are not generally available in a large variety of compositions that are close together.

For volumetric experiments, samples are sometimes issued to students in the form of carefully measured volumes of a standard solution. The student dilutes his sample to volume, titrates aliquot portions, and reports the total amount of sought-for substance in the sample issued to him. The experimental directions of this text are easily adapted to analysis of such samples. The advantage of solution samples is that only one standard solution need be used for the whole class; different sample sizes may be obtained by issuing different volumes of the solution. For small classes (less than fifteen students) preparation and dispensing are probably easier for solution samples than for solid samples; but for large classes the reverse is true.

SUPPLEMENTARY QUESTIONS

Sections 16A, B

S1. In the region just after the equivalence point of Fig. 16.2 (p. 277), AgCl exists in the presence of excess AgNO_3 , and Ag^+ is adsorbed. Consider the fate of a small amount of added AgNO_3 , and show that the true $p\text{Ag}$ curve lies above that of Fig. 16.2. Repeat these considerations for the region just before the equivalence point. These considerations indicate that adsorption decreases the slope of the titration curve in the region of the equivalence point (L12).

S2. Mercurous ion (Hg_2^{2+}) may be titrated with standard NaCl to form insoluble Hg_2Cl_2 . Where does the point of maximum slope fall in relation to the equivalence point?

S3. In carrying out a high-precision titration by the method of equal turbidity, devise a method of measuring the amounts of sample and standard solution with higher precision than is possible with ordinary student equipment.

S4. Consider what happens when standard AgNO_3 is added before and after the equivalence point in the titration of NaCl , and explain why the conductivity should change at different rates before and after the equivalence point.

S5. Describe briefly how NaCl might be titrated conductometrically with standard AgNO_3 . Explain how the end point is established.

S6. Under what conditions would the wings of the titration curve of Fig. 16.1 (p. 275) approach straight lines?

S7. The solubilities of the silver salts of some fluorescein derivatives decrease in the following order: fluorescein, dichlorofluorescein, eosin (tetrabromofluorescein), diiodofluorescein, erythrosin (tetraiodofluorescein). Give the order of increasing adsorbability of the dyes on AgCl in the presence of excess Ag^+ .

S8. Explain the affinity of AgCl particles for nitrobenzene. (Hint: Nitrobenzene is polar.)

Section 16C

S1. In the determination of fluoride as PbClF , explain why (a) the precipitate is soluble in dilute HNO_3 , and (b) the method is not highly accurate.

S2. Considering that Ag mercaptides are insoluble in dilute acid, what must be the order of magnitude of the solubility products?

S3. Why are precipitation reactions often nonstoichiometrical? In such cases, what is the best way to standardize the standard solution?

S4. Describe specifically the reactions that occur along the various portions of the titration curves of Fig. S16.1 (p. 760).

S5. The sharp corners shown on the theoretical curves of Fig. S16.1 are rounded on the corresponding experimental curves. Explain.

S6. Alter the titration curve of Fig. S16.1 to show the error resulting from the coprecipitation of AgCl at the first end point.

S7. How would the titration curve of Fig. S16.1 be altered if (a) the sample contained NaBr instead of NaI, (b) the sample contained NaBr instead of NaCl, (c) the sample contained 0.2 M NaI instead of 0.1 M.

S8. Plot approximately the analog of Fig. 16.1 for the NaI-NaCl titration of Fig. S16.1. Plot $[Ag^+]$, $[I^-]$, and $[Cl^-]$.

SUPPLEMENTARY PROBLEMS

Sections 16A, B

S1. Show that the inflection point for the Ag^+-Cl^- titration of Fig. 16.2 (p. 277) comes at the equivalence point.

S2. In the titration represented by Table 16.1 (p. 276) the standard $AgNO_3$ is added in 0.025 ml (i.e., one-half drop) increments near the equivalence point. Calculate the amount of AgCl that precipitates in each of the following intervals in the titration: (a) 49.950 to 49.975, (b) 49.975 to 50.000, (c) 50.000 to 50.025, (d) 50.025 to 50.050 ml of standard $AgNO_3$. To save time in computation, use the data of Table 16.1 as much as possible. Is there a definite point corresponding to the cessation of further precipitate formation?

S3. The titration represented by Fig. 16.2 is carried out by the method of equal turbidity. At a point before the end point, two 1.0-ml portions of the clear supernate from the titrated solution are withdrawn. To one portion, 1.0 ml of 0.0010 M NaCl is added, and to the other portion, 1.0 ml of 0.0010 M $AgNO_3$ is added. The $AgNO_3$ produces twice as much turbidity (i.e., twice as much AgCl) as the NaCl. How close to the equivalence point is the titrated solution?

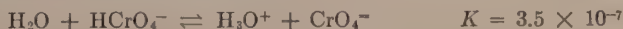
Ans. 0.014% before the eq. pt. (0.007 ml of 0.1 M $AgNO_3$).

S4. In the titration of 50.00 ml of 0.1000 M NaBr with 0.1000 M $AgNO_3$, what range of K_2CrO_4 indicator concentrations could be used to form a precipitate within 0.2% of the equivalence point?

S5. Correct the answer to Ex. 2, page 282, for activity effects. Explain qualitatively why the end-point error increases with ionic strength.

Ans. 0.042 ml of 0.1 M $AgNO_3$, or 0.08%.

S6. Chromate forms a weak acid:



Find $[CrO_4^{2-}]$ in 0.0020 M K_2CrO_4 at pH values of 5.00, 6.00, and 7.00. What would be the end-point error in Ex. 2, page 282, if the end-point pH were 6.00? (Show that formation of $Cr_2O_7^{2-}$ may be ignored without serious error in this problem.)

S7. A 50.00-ml portion of 0.1000 M KIO_3 is titrated with 0.1000 M $AgNO_3$. (a) What range of K_2CrO_4 indicator concentrations could be used to form a pre-

precipitate within 0.2% of the equivalence point? (b) Explain the shortcomings of this titration.

Ans. (a) 2.4×10^{-5} to $7.3 \times 10^{-5} M$. (b) Slope of titration curve too gradual. Indicator concentration too low and too critical.

S8. Repeat Prob. S7, using K_2X as an indicator (K_s for Ag_2X is 1.00×10^{-10}). Even though the range is narrow and restricted, it might be possible to find such an indicator and to control its concentration. Even so, however, it would not give a good end point. Explain. (Hint: If the indicator-ion concentration is selected to exceed the solubility product of Ag_2X at 0.2% before the equivalence point, consider the degrees of supersaturation under which the indicator precipitate would have to form over the interval within 0.2% of the equivalence point.)

S9. Show that $AgCl_2^-$ formation has no significant effect on the titration curve of Fig. 16.2. (Hint: Show that for the values of pAg and pCl calculated in Table 16.1, the equilibrium concentration of $AgCl_2^-$ is too low to affect the values.)

Ans. $[AgCl_2^-] = 1.3 \times 10^{-6} M$, at 10 ml of $AgNO_3$.

S10. I^- is adsorbed much more efficiently than Ag^+ by AgI . Hence, in the titration of NaI with $AgNO_3$, the isoelectric point (that point where the AgI adsorbs no excess of either I^- or Ag^+ , and is neutral) comes after the equivalence point. The isoelectric point occurs when $[Ag^+]$ is about 10^4 -fold higher than $[I^-]$ (K11). When an adsorption indicator is used for this titration, the end point occurs near the isoelectric point, for it is in passing through this point that the AgI changes from a negatively charged colloid that cannot adsorb the indicator ion to a positively charged one that can. Compute the end-point error in the titration of 0.1000 M NaI with 0.1000 M $AgNO_3$, when an adsorption indicator is used.

S11. Approximately what must $[Fe^{3+}]$ be, in order that the back titration in the Volhard determination of chloride may be made without removing $AgCl$, and without end-point error? The feasibility of this method is described by Swift and co-workers (S37). Assume that $[FeSCN^{2+}]$ must be $6.4 \times 10^{-6} M$ for a perceptible end-point color. See Appendices V and X for the appropriate equilibrium constants. Hint: Note that at the equivalence point

$$\left(\begin{array}{c} \text{Total } Ag^+ \\ \text{in soln.} \end{array} \right) = \left(\begin{array}{c} \text{total } Cl^- \\ \text{in soln.} \end{array} \right) + \left(\begin{array}{c} \text{total } SCN^- \\ \text{in soln.} \end{array} \right)$$

$$[Ag^+] = [Cl^-] + [SCN^-] + [FeSCN^{2+}]$$

Ans. 0.095 M .

S12. As the result of an experimental study, Swift recommends a value of 0.20 M for $[Fe^{3+}]$ in Prob. S11. Assuming that the equilibrium-constant values of Prob. S11 are correct, what would be the end-point error in using Swift's value of 0.20 M for $[Fe^{3+}]$?

Section 16C

S1. Verify the pAg , pCl , and pI values in Fig. S16.1 (p. 760) when the following volumes of $AgNO_3$ are added: 49.50, 49.95, 50.05, 50.50, 95.00, 99.95, 100.00, 100.05, 105.00 ml.

S2. Note that over the whole range of Fig. S16.1, $pAg + pSCN = 16$. Derive this relationship from the solubility-product expression. Find the region over which $pAg + pCl = 10$, and explain. Find the region over which $pI - pCl = 6$, and explain.

S3. In the titration shown in Fig. S16.1, it is desired to use 0.030 M B^- as an indicator for the iodide equivalence point. Within what range of values must the

solubility product of the indicator precipitate (Ag_2B) fall, in order that the end-point error may be less than 0.1%? *Ans.* 1.2×10^{-25} to 1.2×10^{-19} .

S4. The silver salt of an organic acid, AgA , has a solubility product of 1.0×10^{-6} , and the end point in the direct titration of 0.1 M NaA with 0.1 M AgNO_3 is quite poor. Outline an indirect argentimetric procedure for titration of 25-ml portions of 0.1 M NaA , in which the relative error due to solubility losses will be less than 0.1%. Describe calculations, and estimate the error of the procedure.

Stoichiometrical problems in precipitation titrations

S1. The fluoride in a 1.72-g sample is converted quantitatively to PbClF , which is dissolved in acid and titrated indirectly for chloride by the Volhard method. After addition of 42.40 ml of 0.1000 M AgNO_3 , 0.69 ml of 0.1017 M KSCN are required for back titration. Calculate the % F in the sample. *Ans.* 4.61%.

S2. An excess of 50.00 ml of 0.1000 M AgNO_3 is added to a sample containing iodoform and other inert substances. After precipitation is complete, titration of the excess AgNO_3 requires 13.50 ml of 0.1382 M KSCN . What is the weight of iodoform (CHI_3) in the sample?

S3. A 0.3093-g sample contains only KCl and KClO_3 . After reduction, in which all chlorate is converted to chloride, titration by the Fajans method requires 35.26 ml of 0.1000 M AgNO_3 . Calculate the composition of the original sample. *Ans.* 61.7% KCl .

S4. What molarity of AgNO_3 standard solution is required in order that one milliliter of the solution will represent two per cent of NaCl in a sample when 0.500 g is taken for analysis?

S5. Let S be the grams of sample per 50-ml aliquot in Exp. 16.4, V_A the milliliters of M_A molar AgNO_3 used, and V_K the milliliters of M_K molar KSCN used. Derive a general equation for calculating the % Cl in the sample. *Ans.* $3.5453 (V_A M_A - V_K M_K) / S$.

S6. If 0.3000 M KSCN is used, what weight of Ag alloy should be taken for a Volhard titration, to ensure that each milliliter of KSCN represents two per cent of Ag in the sample?

S7. A 1.000-g sample consists of ZnCl_2 and alkali chlorides. It is dissolved, and ZnS is precipitated. The precipitate is filtered, washed, and treated with a 50.00-ml portion of 0.1000 M AgNO_3 . The Ag_2S is filtered off, and the residual Ag^+ left in the filtrate is titrated with 0.0500 M KSCN , 5.76 ml being required. What is the Zn content of the sample, as % ZnCl_2 ? *Ans.* 32.11%.

ACID-BASE EQUILIBRIA

BUFFER COMPOSITION FOR MAXIMUM BUFFERING ACTION

(See Sec. 17E.2, p. 322)

Suppose that an aqueous solution contains a moles of a weak monoprotic acid (HA), and that NaOH is slowly added. At any point, let b be the moles of NaOH added. If b is less than a , the base neutralizes a part of the acid, so that $a - b$ is the moles of acid left, and b is the moles of NaA formed. If v is the volume of solution, in liters, the total concentration of HA is $(a - b)/v$, and the total concentration of NaA is b/v .

An expression for pH in terms of a and b may now be derived. Assuming that the ionization of HA is slight, $[HA] = (a - b)/v$, and $[A^-] = b/v$. Then

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]} = K_a \frac{(a - b)/v}{b/v} = K_a \left(\frac{a}{b} - 1 \right)$$

$$pH = -\log [H_3O^+] = -\log K_a - \log \left(\frac{a}{b} - 1 \right)$$

The rate of change of pH with respect to added base is a minimum when $d^2(pH)/db^2 = 0$. Differentiating the expression for pH gives

$$\frac{d(pH)}{db} = \frac{a}{2.303b(a - b)}$$

$$\frac{d^2(pH)}{db^2} = \frac{a(2b - a)}{2.303b^2(a - b)^2}$$

Setting $d^2(pH)/db^2$ equal to zero gives $b = a/2$, when $d(pH)/db$ is a minimum. At this point, the total moles of NaA is b , or $a/2$, and the total moles of HA is $a - b$, or $a/2$. In other words, $d(pH)/db$ is a minimum, and buffering action is a maximum when the amounts (and therefore concentrations) of acid and salt are equal.

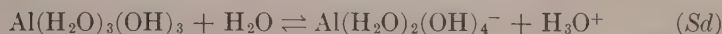
The actual value of $d(pH)/db$ at the minimum may be found to be $4/(2.303a)$, showing that the buffering action increases with the concentration of acid and salt.

HYDROLYSIS OF METAL IONS

(See Sec. 17F, p. 325)

The hydrolysis of metal ions is referred to repeatedly in other parts of this text, in connection with (1) contamination of precipitates (pp. 203, 724), (2) errors in precipitation titrations (pp. 296, 299, 306), and (3) interference by metal ions in acid-base titrations (p. 789), and in preparation of standard cerate solutions (p. 478).

It is not necessary to regard this behavior as hydrolysis; more properly, it should be called *protolysis*. In Brönsted terms, the hydrated forms of such metal ions are conceived to be polyprotic acids that ionize in steps. Thus the behavior of aluminum is as follows:



$\text{Al}(\text{H}_2\text{O})_6^{3+}$ is a moderately strong acid. Thus, 0.1 M AlCl_3 has a pH around 3. In a solution of an aluminum salt, an appreciable proportion of the aluminum exists in the hydroxy form. As the acidity of the solution decreases, higher hydroxy complexes are formed, until eventually the insoluble hydroxide precipitates (Eq. Sc). Equation Sd describes the solubility of aluminum hydroxide in basic solutions. Ferric ion and other metal ions that precipitate at low pH behave similarly, though not all of them are soluble in basic solutions.

Pokras (P7) has reviewed the behavior of aquated metal ions.

TREATMENT OF MULTIPLE EQUILIBRIA

(See Sec. 17G.2, p. 328)

The algebra of multiple-equilibrium systems may be highly complex. In treating such systems the worker faces a dilemma. If he wishes to be rigorous and to make no guesses or approximations, the resulting equations may be too difficult to solve. On the other hand, if approximations are made to simplify the equations, the answer may be inaccurate. It is therefore necessary to compromise between rigor and approximations. There is nothing wrong with guessing or approximating;

this is a formal part of the scientific method, and is done by all workers in all fields. It must be remembered, however, that all approximations must be tested in the light of the answers obtained.

Two approaches for handling multiple equilibria are outlined in the following sections. Both approaches are the same in principle, but they differ at the points where the approximations are made. The *numerical method* is generally preferred whenever a numerical answer is desired for a problem. Approximations and simplifying assumptions are made at the outset, and are then tested after the answer is obtained. The *general method* gives a general equation (or set of equations) relating $[\text{H}_3\text{O}^+]$ to composition and equilibrium constants, and is useful whenever the general dependence of $[\text{H}_3\text{O}^+]$ on these parameters is sought.

The Numerical Method

Many different kinds of aqueous acid-base systems may be handled by the following method of approximations (K4). In working any problem, it is helpful to keep constantly in mind the relative strengths and concentrations of the various acids in the system; these relationships sometimes indicate approximations or assumptions that may greatly simplify the numerical work.

1. Specify the composition of the solution by writing the total concentration of each acid and salt present.

2. Write the minimum number of chemical equilibria describing the system, together with the equilibrium-constant expressions for each. These equilibria must be independent; that is, no one may be derivable simply by combining or rearranging the other equilibria. These equations consist of all the stepwise ionization constants of each acid, and the ionization expression for water. Thus, an aqueous solution of NaAc, Na_2HPO_4 , HCN, and HCl would be describable by the ionization equations for the following six acids: HAc, H_3PO_4 , H_2PO_4^- , HPO_4^{2-} , HCN, and H_2O . (HCl is a strong acid and is not describable by an ionization constant.)

3. Carry out the hypothetical process of removing all acidic H^+ from all the acids (except water). The total H^+ thus removed is symbolized by R_{H} , in moles per liter. This H^+ is theoretically made to react with the several bases that remain. It reacts first with the strongest base; any remaining H^+ then reacts with weaker and weaker bases until equilibrium is reached. At this point the solution attains the sought-for composition.

Successive estimations must be made in combining the removed H^+ with the bases. An estimate of $[\text{H}_3\text{O}^+]$ is made, which determines the H^+ that combines with each base. The first estimate of $[\text{H}_3\text{O}^+]$ is often

simply a guess. From this estimate of $[\text{H}_3\text{O}^+]$, the concentrations of all species may be estimated. Then, in turn, the sum of H^+ in all the H^+ -bearing species may be estimated; this sum is represented by S_{H} . From a material balance on H^+ , we obtain

$$R_{\text{H}} = S_{\text{H}} + [\text{H}_3\text{O}^+] - [\text{OH}^-]$$

since $[\text{H}_3\text{O}^+] - [\text{OH}^-]$ represents the free H^+ in solution in excess of that contributed by the ionization of water. Unless the $p\text{H}$ is close to 7, either $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ is negligible. In many cases, $[\text{H}_3\text{O}^+] - [\text{OH}^-]$ is negligible.

If the first estimate of $S_{\text{H}} + [\text{H}_3\text{O}^+] - [\text{OH}^-]$ is significantly different from R_{H} , a second estimate of $[\text{H}_3\text{O}^+]$ is made. If there is still a significant difference between R_{H} and the second estimate of $S_{\text{H}} + [\text{H}_3\text{O}^+] - [\text{OH}^-]$, third estimates must be made, and so on, until there is no significant difference. At this point the correct composition of the solution has been estimated.

4. The method so far has been described for the case in which only H^+ is removable, and in which there are no OH^- -bearing species. If there are OH^- -bearing substances in the original solution, then R_{H} is the sum of removed H^+ minus removed OH^- , in moles per liter. A negative R_{H} simply means that the removable OH^- exceeds the removable H^+ . Similarly, after recombination of the H^+ , some OH^- -bearing substances may exist. S_{H} is then the sum of the concentrations of the H^+ -bearing species minus the sum of the concentrations of the OH^- -bearing species. A negative value for S_{H} simply means that OH^- -bearing species preponderate over H^+ -bearing ones. This modification is only one way to handle OH^- -bearing substances. The student may wish to devise others.

Example. Calculate $[\text{H}_3\text{O}^+]$ in a solution containing 0.050 M NaH_2PO_4 , 0.030 M Na_2HPO_4 , 0.080 M HOCl , and 0.040 M NaAc .

The independent equilibria are:



$$R_{\text{H}} = \underset{\text{From } \text{NaH}_2\text{PO}_4}{2(0.050)} + \underset{\text{From } \text{Na}_2\text{HPO}_4}{0.030} + \underset{\text{From } \text{HOCl}}{0.080} = 0.210 \text{ } M \quad (g)$$

First estimate: $[\text{H}_3\text{O}^+] = 10^{-8} M$. The concentrations of the various H^+ -bearing species may be calculated as follows.

For the HAc species:

$$\frac{[\text{Ac}^-]}{[\text{HAc}]} = \frac{1.76 \times 10^{-5}}{[\text{H}_3\text{O}^+]} = \frac{1.76 \times 10^{-5}}{(10^{-8})} = 1760 \quad (h)$$

This indicates that $[\text{HAc}]$ is negligible compared to $[\text{Ac}^-]$ and therefore also to R_{H} .

For the HOCl species:

$$\frac{[\text{OCl}^-]}{[\text{HOCl}]} = \frac{3.2 \times 10^{-8}}{[\text{H}_3\text{O}^+]} = \frac{3.2 \times 10^{-8}}{(10^{-8})} = 3.2 \quad (i)$$

$$[\text{HOCl}] + [\text{OCl}^-] = 0.080 M \quad (\text{Material balance on hypochlorite}) \quad (j)$$

Eqs. *i* and *j* may be solved for $[\text{HOCl}]$, giving

$$[\text{HOCl}] = 0.0190 M \quad (k)$$

For the phosphate species:

$$\frac{[\text{H}_2\text{PO}_4^-]}{[\text{H}_3\text{PO}_4]} = \frac{K_1}{[\text{H}_3\text{O}^+]} = \frac{7.1 \times 10^{-8}}{(10^{-8})} = 7.1 \times 10^5 \quad (l)$$

$$\frac{[\text{HPO}_4^-]}{[\text{H}_2\text{PO}_4^-]} = \frac{K_2}{[\text{H}_3\text{O}^+]} = \frac{6.2 \times 10^{-8}}{(10^{-8})} = 6.2 \quad (m)$$

$$\frac{[\text{PO}_4^{3-}]}{[\text{HPO}_4^-]} = \frac{K_3}{[\text{H}_3\text{O}^+]} = \frac{4.4 \times 10^{-13}}{(10^{-8})} = 4.4 \times 10^{-5} \quad (n)$$

Eqs. *l* and *n* indicate that $[\text{H}_3\text{PO}_4]$ and $[\text{PO}_4^{3-}]$ are negligible, leaving H_2PO_4^- and HPO_4^- as the only important phosphate species in solution. Neglecting the unimportant species, a material balance on the phosphate introduced as NaH_2PO_4 and Na_2HPO_4 gives

$$[\text{H}_2\text{PO}_4^-] + [\text{HPO}_4^-] = 0.080 M \quad (o)$$

Eqs. *m* and *o* may be solved, giving

$$[\text{H}_2\text{PO}_4^-] = 0.0111 M \quad (p)$$

$$[\text{HPO}_4^-] = 0.0689 M \quad (q)$$

Summing the H^+ -bearing species, the first estimate of $S_{\text{H}} + [\text{H}_3\text{O}^+] - [\text{OH}^-]$ is

$$0.0190 + 2(0.0111) + 0.0689, \text{ or } 0.1101 M$$

From HOCl	From H_2PO_4^-	From HPO_4^-
--------------	-----------------------------------	--------------------------

This is far below the R_{H} value of $0.210 M$, indicating that the next estimate of $[\text{H}_3\text{O}^+]$ must be raised.

A second estimate of $[\text{H}_3\text{O}^+]$ as $10^{-7} M$ gives a value for $S_{\text{H}} + [\text{H}_3\text{O}^+] - [\text{OH}^-]$ of $0.1900 M$, still considerably below the R_{H} value of 0.210 .

Further estimates result in a value of $2.00 \times 10^{-7} M$ for $[\text{H}_3\text{O}^+]$.

As a matter of further interest, once $[\text{H}_3\text{O}^+]$ is known, the concentrations of all other species may be found with the aid of the preceding equations.

The General Method

In outline, the general method consists of the following steps.

1. Write the independent equilibria (p. 770) and their equilibrium constants. As an example, for an aqueous solution containing C_p M H_3PO_4 and C_a M HAc , the independent equilibria consist of the three stepwise ionizations of H_3PO_4 , the ionization of HAc , and the ionization of water, which give five equations involving eight (unknown) concentrations: $[H_3PO_4]$, $[H_2PO_4^-]$, $[HPO_4^{=}]$, $[PO_4^{=}]$, $[HAc]$, $[Ac^-]$, $[H_3O^+]$, and $[OH^-]$.

2. More equations may be obtained by writing material balances on each of the solutes. Thus for the solution above, material balances on phosphate and acetate give, respectively,

$$C_p = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{=}] + [PO_4^{=}]$$

$$C_a = [HAc] + [Ac^-]$$

At this point the number of equations is one less than the number of unknown concentrations. In the case of the foregoing H_3PO_4 - HAc solution, there are seven equations and eight unknowns.

3. The remaining equation may be obtained by applying the principle of electroneutrality, which states that the sum of the charges on the anions in the solution must equal the sum of the charges on the cations. For the H_3PO_4 - HAc solution mentioned above, the equation is

$$[H_3O^+] = [H_2PO_4^-] + 2[HPO_4^{=}] + 3[PO_4^{=}] + [Ac^-] + [OH^-]$$

Another way of obtaining the remaining equation is to carry out a material balance on H^+ (or OH^-), as expressed in the equation $R_H = S_H + [H_3O^+] - [OH^-]$ on page 771. For the above H_3PO_4 - HAc solution this gives

$$3C_p + C_a = 3[H_3PO_4] + 2[H_2PO_4^-] + [HPO_4^{=}] + [HAc] + [H_3O^+] - [OH^-]$$

Which of the two methods is more advantageous depends upon the particular case. For the above H_3PO_4 - HAc solution, the electroneutrality equation is better. Significant figures may be lost if the H^+ -balance equation is not properly employed, since for most solutions $3C_p + C_a$ is very nearly equal to $3[H_3PO_4] + [HAc]$.

4. The proper number of equations to solve for the various concentrations is now available. The equations may have to be left in parametric form if they are too complicated to solve explicitly for $[H_3O^+]$ or for any other unknown concentration. If a numerical answer is desired, approximations must often be used to solve the equations. An example follows.

Example. Give a general expression for $[\text{H}_3\text{O}^+]$ in a solution containing $C_a M$ HA and $C_s M$ NaA.

The independent equilibria are



A material balance on A^- gives

$$C_a + C_s = [\text{HA}] + [\text{A}^-] \quad (c)$$

The electroneutrality principle gives

$$[\text{Na}^+], \text{ or } C_s + [\text{H}_3\text{O}^+] = [\text{A}^-] + [\text{OH}^-] \quad (d)$$

All ion concentrations other than $[\text{H}_3\text{O}^+]$ may be expressed in terms of $[\text{H}_3\text{O}^+]$.

$$[\text{OH}^-] = \frac{K_w}{[\text{H}_3\text{O}^+]} \quad (\text{From } b) \quad (e)$$

$$[\text{A}^-] = C_s + [\text{H}_3\text{O}^+] - \frac{K_w}{[\text{H}_3\text{O}^+]} \quad (\text{From } d \text{ and } e) \quad (f)$$

$$[\text{HA}] = C_a - [\text{H}_3\text{O}^+] + \frac{K_w}{[\text{H}_3\text{O}^+]} \quad (\text{From } c \text{ and } f) \quad (g)$$

Substituting f and g into Eq. a gives

$$[\text{H}_3\text{O}^+] = K_a \frac{C_a - [\text{H}_3\text{O}^+] + K_w/[\text{H}_3\text{O}^+]}{C_s + [\text{H}_3\text{O}^+] - K_w/[\text{H}_3\text{O}^+]} \quad (h)$$

Equation h is actually a cubic. If a numerical answer for $[\text{H}_3\text{O}^+]$ must be obtained by approximations, Eq. h is easier to use than the conventional cubic form. Also, Eq. h permits insight into certain approximations. Thus, if $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ is much smaller than C_a or C_s , Eq. h reduces to the simpler forms given in Probs. 11 and 12 (p. 340).

Equation h is perfectly general. When $C_s = 0$, an equation describing ionization in pure HA solutions results. When $C_a = 0$, an equation describing the hydrolysis of pure NaA solutions is obtained. Equation h is more general than Eqs. 17.6 or 17.9. It may be seen that there is no real distinction among the following kinds of solutions: pure HA; mixtures of HA and NaA; pure NaA. That such a distinction appears to exist in the elementary treatment is a consequence of the single-equilibrium approach.

It should be pointed out that a material balance on H^+ could have been used in place of Eq. d .

$$C_a = [\text{HA}] + [\text{H}_3\text{O}^+] - [\text{OH}^-] \quad (d')$$

Note, however, that Eq. c is obtained by adding Eqs. d and d' . Hence only two out of these three equations are independent and useful in solving for the ion concentrations.

CORRECTION FOR ACTIVITY EFFECTS

(See Sec. 17G.3, p. 332)

For many systems, a good estimate of the ionic strength may be made from the original composition of the system alone. In such cases, activity coefficients may be estimated from Appendix VI and written into the equilibrium-constant equations before solving them.

In some systems, however, reactions may occur among the solutes, in which case the ionic strength cannot be estimated from the original composition of the system. For example, the ionic strength of the 0.100 *M* NH_4BO_2 solution discussed on page 328 cannot be estimated at 0.100 *M*; about half of the solute is hydrolyzed to un-ionized NH_3 and HBO_2 , and the ionic strength is only about 0.05 *M*. In such cases, it is generally desirable to estimate $[\text{H}_3\text{O}^+]$ and concentrations of other solute species first, neglecting activity coefficients. Then a first estimate of the ionic strength may be calculated, which in turn allows estimates to be made of the activity coefficients for the various solute species. By using these activity coefficients, second estimates of $[\text{H}_3\text{O}^+]$ and other solute concentrations may be made, after which a second estimate of ionic strength may be made. This process is continued until there is no significant difference between two successive estimates of ionic strength, at which point the solution composition is known. Convergence upon a constant value of ionic strength is usually rapid, and more than two estimates are seldom required.

SUPPLEMENTARY QUESTIONS AND PROBLEMS*Section 17E*

S1. The value of $d(\text{pH})/db$ at maximum buffering action is $4/(2.303a)$, independent of K_a (p. 769). Discuss the significance of this relationship.

S2. A buffer solution consists of a weak acid (HA) and its salt (NaA). How does dilution affect the pH (a) neglecting activity effects, (b) considering activity effects?

S3. Repeat Ques. S2 for a buffer containing the weak base (X) and its salt (XHCl).

S4. The Fe^{3+} in 100 ml of a solution containing 0.010 *M* FeCl_3 and 0.100 *M* HCl is to be precipitated homogeneously, using a formate buffer. (a) Calculate the theoretical amount of urea (plus a 50% excess) needed to precipitate the Fe^{3+} quantitatively. (b) With the amount of urea calculated in part a, specify the formic acid concentration that should be used, in order that the pH will never rise above 4.00.

Section 17F

S1. Give the steps in the ionization of tetraaquo zinc ion, $\text{Zn}(\text{H}_2\text{O})_4^{2+}$.

S2. A solution of AlCl_3 is quite acid because hydrated aluminum ion is a fairly strong acid. When an excess of NaF is added to an AlCl_3 solution, the acidity of the latter decreases greatly. Explain.

S3. Compute the percentage hydrolysis and the pH in 0.100 *M* Na_2CO_3 .

Ans. 4.0%, 11.60.

S4. Can a solution containing NaAc and small concentrations of HAc ever be basic? Give a specific example, and compute the pH.

S5. Use data in Appendix V to estimate the pH of 0.010 M $\text{Fe}_2(\text{SO}_4)_3$. What fraction of the Fe^{3+} exists in the hydrolyzed form? What fraction of the Fe^{3+} exists in the hydrolyzed form at pH 3.00? (Neglect all species other than $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ and $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$.) *Ans.* 2; half; 0.9.

S6. Portions of a particular preparation of CaCl_2 were dissolved in pure water to give solutions of the following concentrations: 0.5, 0.16, 0.1, 0.02, 0.0005 M. The pH values of these solutions were, respectively: 8.1, 7.6, 7.0, 6.7, 6.4. Tell why these data cannot be explained by postulating protolysis of the aquo- Ca^{2+} ion. Postulate an impurity that would explain these data (P7).

Sections 17G, H

S1. Compute $[\text{H}_3\text{O}^+]$ and the concentrations of the various solute species in the following systems: (a) 0.0100 M HAc, 0.0100 M lactic acid; (b) 0.100 M HAc, 0.100 M benzoic acid; (c) 0.100 M NaBO_2 , 0.100 M NaAc; (d) 0.100 M NaBO_2 , 0.100 M NaCN; (e) 0.100 M HAc, 0.100 M NaAc, 0.100 M HBO_2 ; (f) 0.0100 M NaCN, 0.0100 M HAc; (g) 50 ml of 0.100 M formic acid plus 50 ml of 0.100 M NaAc. *Ans.* (a) $[\text{H}_3\text{O}^+] = 0.00126 \text{ M}$; $[\text{Lactate}] = 0.00112 \text{ M}$;

$[\text{Ac}^-] = 1.38 \times 10^{-4} \text{ M}$; $[\text{HAc}] = 0.0099 \text{ M}$; $[\text{HLactate}] = 0.0089 \text{ M}$.

S2. Compute $[\text{H}_3\text{O}^+]$ and the concentrations of the various solute species in the following systems: (a) 0.100 M Na_3PO_4 , 0.050 M HCl; (b) 0.100 M tartaric acid; (c) 0.035 M Na_3PO_4 , 0.196 M Na_2HPO_4 ; (d) 0.100 M $(\text{NH}_4)_2\text{HPO}_4$; (e) 0.100 M $\text{Na}_2\text{C}_2\text{O}_4$, 0.100 M NaHC_2O_4 ; (f) 0.100 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$; (g) 0.050 M citric acid. *Ans.* (a) $[\text{H}_3\text{O}^+] = 7.5 \times 10^{-13} \text{ M}$;

$[\text{OH}^-] = 0.0133 \text{ M}$; $[\text{PO}_4^{=}] = 0.0367 \text{ M}$; $[\text{HPO}_4^-] = 0.0633 \text{ M}$.

S3. When distilled water comes into equilibrium with the atmosphere, the total CO_2 concentration in solution is 0.000014 M. Compute the pH of the water. Would 0.010 M CaCl_2 be stable or unstable in air with respect to precipitation of CaCO_3 ? *Ans.* 5.69; stable.

S4. Calculate the solubility of CaCO_3 in a solution buffered at pH 7.00.

S5. Calculate the molar solubility of PbC_2O_4 in 0.100 M HNO_3 . *Ans.* $3.5 \times 10^{-4} \text{ M}$.

S6. Using K_a for HCN, K_s for $\text{Ag}_2(\text{CN})_2$, and the stability constant for $\text{Ag}(\text{CN})_2^-$, prove that moderate concentrations of cyanide (0.001 M) interfere even in the Volhard method for chloride, where $[\text{H}_3\text{O}^+] = 0.10 \text{ M}$.

S7. Give the general expression for $[\text{OH}^-]$ in C M B. Give the form to which this equation reduces when (a) $[\text{OH}^-] \gg [\text{H}_3\text{O}^+]$, (b) $[\text{H}_3\text{O}^+] \ll [\text{OH}^-] \ll C$.

$$\text{Ans. } K_b \frac{C - [\text{OH}^-] + K_w/[\text{OH}^-]}{[\text{OH}^-] - K_w/[\text{OH}^-]}; \quad (a) \sqrt{K_b(C - [\text{OH}^-])}; \quad (b) \sqrt{K_b C}.$$

S8. Give the general expression for $[\text{H}_3\text{O}^+]$ in C M H_2A . Give the form to which this equation reduces when (a) $[\text{OH}^-] \ll [\text{H}_3\text{O}^+]$, (b) $[\text{OH}^-] \ll [\text{H}_3\text{O}^+] \ll C$, (c) $K_2 \ll K_1$.

S9. (a) Express the molar solubility (s) of BaSO_4 in dilute HCl solution as a function of $[\text{H}_3\text{O}^+]$. Let K_s be the solubility product of BaSO_4 , and let K_2 be the ionization constant for HSO_4^- . Assume that $\text{Ba}(\text{HSO}_4)_2$ is soluble, and ignore activity effects. (b) Consider the limiting forms of this equation when $[\text{H}_3\text{O}^+] \gg K_2$, and when $[\text{H}_3\text{O}^+] \ll K_2$, and give the form of a plot of ps against pH. (c) Calculate

the solubility of BaSO_4 in 1.0 M HCl , and compare it with the solubility in water.

Ans. (a) $s = \sqrt{K_s(1 + [\text{H}_3\text{O}^+]/K_2)}$.

S10. (a) Express the molar solubility of BaCO_3 in dilute HCl solution as a function of $[\text{H}_3\text{O}^+]$. Let K_s be the solubility product of BaCO_3 , and let K_1 and K_2 be the ionization constants for H_2CO_3 . Assume that $\text{Ba}(\text{HCO}_3)_2$ is soluble, that no CO_2 escapes from the solution, and ignore activity effects. (b) Give the form of a plot of ps against pH .

Ans. (a) $s = \sqrt{K_s(1 + [\text{H}_3\text{O}^+]/K_2 + [\text{H}_3\text{O}^+]/K_1K_2)}$.

S11. Calculate the neutral point pH in 0.10 M KClO_4 at 25°C . *Ans.* 6.88.

S12. Explain why the concentration constant (p. 701) varies much less with ionic strength for a base like acetate than for a base like ammonia.

S13. For the conditions of Fig. 17.1 (p. 334), show that the fraction of the total carbonate that exists as HCO_3^- is a maximum when $[\text{H}_3\text{O}^+] = \sqrt{K_1K_2}$, or when the pH is 8.34.

S14. Prepare a plot similar to Fig. 17.1 that shows the distribution of phosphate-bearing species as a function of pH .

ACID-BASE TITRATIONS

RECORDED pH TITRATION CURVES

(See Sec. 18B.1, p. 350)

Recording pH meters are available that give a chart record of the pH of a solution as a function of time. If titrant is run into a solution at a constant rate, a titration curve will be traced out directly on the chart record, with pH as ordinates and time (i.e., volume of titrant) as abscissae (see Fig. S18.1, p. 781).

With somewhat greater complexity in apparatus, even further saving in effort is possible. For example, differentiators exist that can be combined with a pH meter to give an output proportional to the time rate of change of pH . In other words, a first derivative of the titration curve can be recorded. The derivative of an S-shaped curve is a peak-shaped one whose maximum comes at the equivalence point (Fig. S18.1). It is much easier to pick out the maximum of the derivative curve than it is to pick out the inflection point.

For a good end point, the peak is so sharp that it is practically a pulse. The end-point pulse may be used to initiate further automatic operations, such as: to turn off and refill an automatic zero buret; or to drain the titration vessel, flush, and add the next sample from an automatic pipet.

ACID-BASE INDICATORS

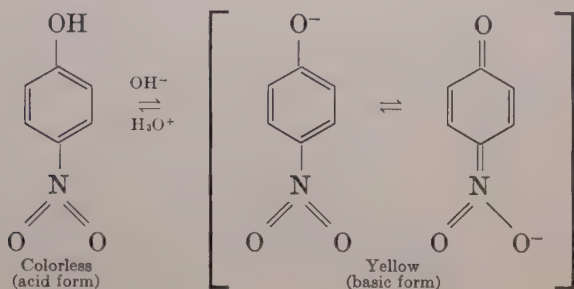
Structure and Mechanism of the Color Change

(See Sec. 18B.2a, p. 352)

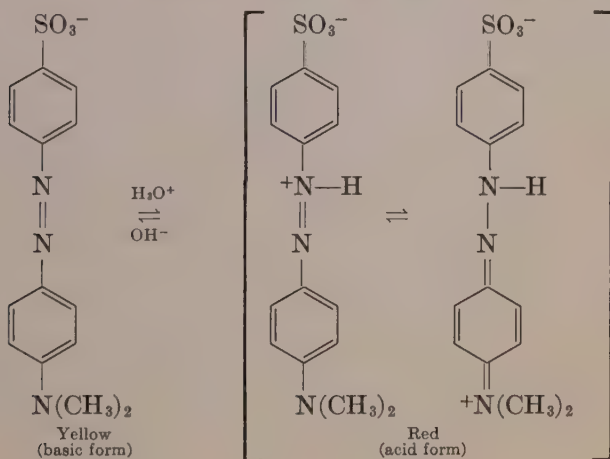
Indicators—highly colored organic substances with fairly complex structures—are described on page 756. When an acid-base indicator loses or gains a proton, there is a rearrangement in the electronic structure (i.e., in the bonding and conjugation), and a consequent change in the absorption and color (C8, W5). These reactions are ionic, involving only shifts of protons and electrons. The color transitions therefore occur more rapidly than in those organic reactions that involve rearrange-

ment of atoms within the molecule, or fragmentation or joining of molecules.

One of the simplest indicators is para-nitrophenol ($pK_I = 6$), the behavior on ionization being



Methyl orange is colored in both acidic and basic forms. The sulfonate group ($-\text{SO}_3^-$) increases the water solubility of the basic form.

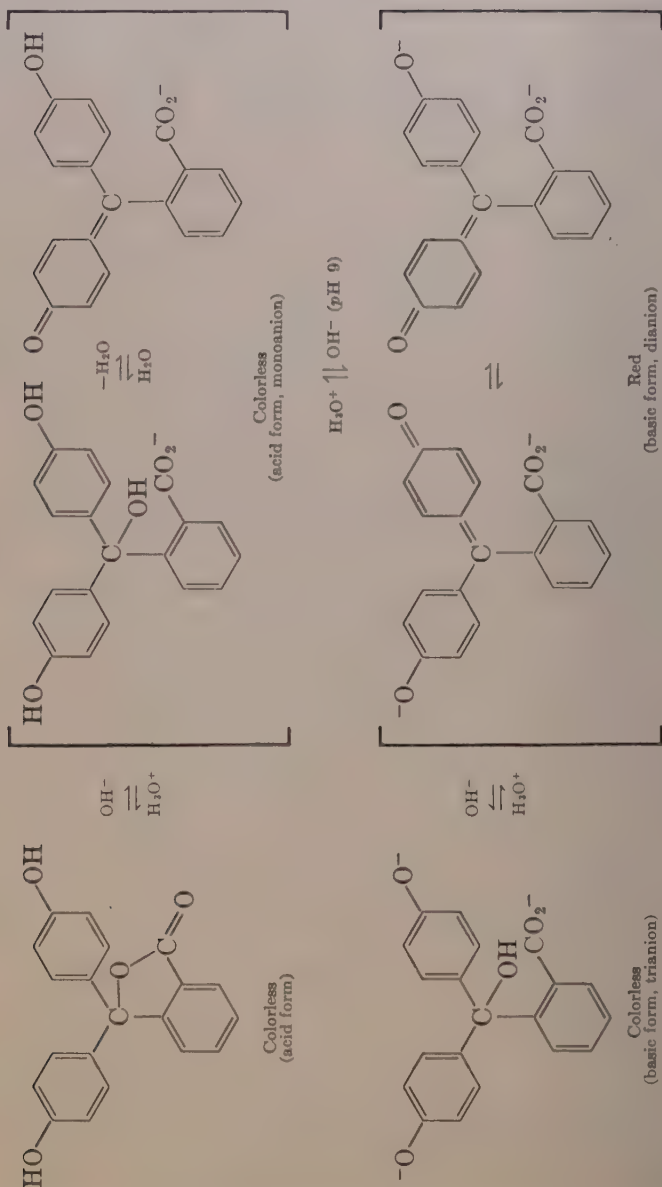


Phenolphthalein is red only at an intermediate pH , being colorless in both acidic and strongly basic solutions (see structural equations on page 780).

Some Factors That Affect the Transition Range of Acid-Base Indicators

(See Sec. 18B.2b, p. 353)

1. The transition range extends only approximately over two pH units. An indicator that has highly different acidic and basic colors



may have a wider transition range than an indicator whose acidic and basic colors are not so different. Also, not all indicator equilibria are so simple as is intimated on page 352. Some indicators transit from the acidic to the basic color through an intermediate form. Some indicators are diequivalent acids or bases and may show two transition ranges.

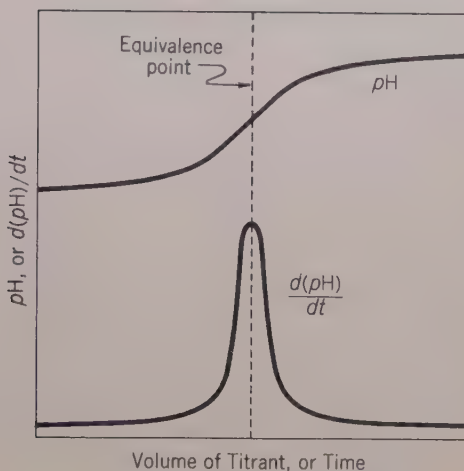
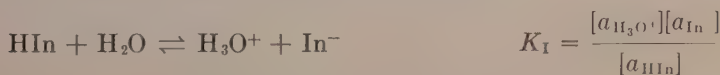


FIG. S18.1. Recorded Titration Curves

2. The sensitivity of the eye is different for different hues, and it may be possible to detect a smaller proportion of the acidic color against a background of the basic color than vice versa, in which case the transition range is not symmetrical about pK_I .

3. According to Eq. 18.4 (p. 353), the transition range is independent of indicator concentration. This is approximately true for a two-color indicator, but not for a one-color indicator. A one-color indicator does not transit from one color to another, but rather the color intensity varies through the transition range. One extreme of the range is marked by the lowest concentration of the colored form that is detectable by the eye. This limiting color will be observed more easily when the total indicator concentration is high. Therefore, the transition range depends not only upon the pH of the solution but also upon the total indicator concentration. Phenolphthalein is such an indicator.

4. The ionization of a simple indicator like p -nitrophenol may be more accurately written in terms of activities.



$$[a_{\text{H}_3\text{O}^+}] = K_I \cdot \frac{[\text{HIn}]}{[\text{In}^-]} \cdot \frac{[\gamma_{\text{HIn}}]}{[\gamma_{\text{In}^-}]}$$

$$pa_{\text{H}}^* = -\log K_I - \log \frac{[\text{HIn}]}{[\text{In}^-]} - \log \gamma_{\text{HIn}} + \log \gamma_{\text{In}^-}$$

*The " pH " that is measured on a pH meter is really a $pa_{\text{H}_3\text{O}^+}$ (i.e., pa_{H}).

For the acidic color of the indicator, the pa_H corresponds to a ratio of 10 for $[HIn]/[In^-]$. The activity coefficients are calculable from the ionic strength (Prob. S8, p. 714) giving

$$(pa_H)_{\text{acid color}} = pK_I - 1 - 0.5 \sqrt{\mu}$$

Similar considerations apply to the pa_H corresponding to the basic color, and the transition range is therefore dependent upon the ionic strength. For moderate variations in ionic strength, the transition ranges of most indicators vary by a few tenths of a pH unit or less (L2).

5. Any factor that affects the equilibrium constant K_I will affect the transition range. Thus, the transition ranges for some (but not all) indicators are markedly temperature dependent. Also, a change in the solvent may affect the ionization of an indicator greatly. In an alcoholic solution, the transition range of an indicator may differ by several pH units from its range in water.

6. An indicator adsorbed upon the surface of a colloid may have a different color from that of the indicator in the bulk of the solution. The color change may be caused by several different mechanisms (L2). This is how some acid-base indicators can act as adsorption indicators in precipitation titrations (p. 758).

Mixed, Fluorescent, and Turbidity Indicators

When the acidic and basic colors of an indicator are not in sharp contrast, the end-point change may not be easy to see. With such an indicator, the end-point change may be made more perceptible by the addition of a second indicator or dye whose color is complementary at the desired pH . At this pH , the mixture passes through a neutral gray. Furthermore, such a mixture transits through the neutral gray region over a pH interval much smaller than the usual two units for the single indicator. Mixed indicators not only render an end point sharper and more perceptible, but also permit titration to a certain pH without the use of comparison solutions.

A good example of a mixed indicator is bromocresol green and methyl red. The acidic and basic colors of the mixture are orange and green, respectively. At pH 5.1, bromocresol green alone is green-blue, and methyl red alone is orange; these two colors are complementary (p. 507), and their mixture is therefore gray at pH 5.1. Similarly, a mixture of methyl orange and xylene cyanole FF (a blue dye that is not an indicator) gives a gray color around pH 3.8. Kolthoff and Stenger list many mixed indicators with transition points from pH 3.2 to 10.8 (K19).

Some weak organic acids fluoresce in the salt (i.e., base) form but not

in the acid form (or vice versa). Some bases behave similarly. When used as indicators, such substances transit from a nonfluorescent to a fluorescent state instead of undergoing a color change. Fluorescent indicators are sometimes useful in colored or turbid solutions that mask the color changes of ordinary acid-base indicators. Walton describes simple apparatus for titrating with fluorescent indicators, and lists several indicators in the pH range 0–10 (W5).

Another class of indicators includes weak organic acids that are insoluble in the acid form, but soluble in the salt form. These may be used as precipitation indicators in acid-base titrations. Solutions of such indicators pass from clear to turbid as the pH decreases through the transition range. Some bases behave similarly. Although the transition range is very narrow for some indicators, it is also critically dependent upon conditions. Turbidity indicators are therefore of limited usefulness. Kolthoff and Stenger summarize the theory of the transition, and list some indicators useful over the pH range 9.0–11.5 (K19).

CALCULATION OF THE ERROR IN TITRATION TO A FIXED pH

(See Sec. 18C.1a, p. 356)

A determinate error results if the end-point pH does not correspond to the equivalence-point pH . The following example illustrates how the magnitude of the error may be calculated. If the acid or base being titrated is rather weak, the error may be appreciable.

Example. An end-point pH of 9.80 is selected for the titration of 50.00-ml aliquots of 0.1 M HA ($K_a = 1.00 \times 10^{-7}$) with 0.1 M NaOH, under the conditions of Fig. 18.3 (p. 345). However, the HA concentration in a series of samples drops to about 0.01 M , and the worker decides to use 0.01 M NaOH for titration. What is the error in titrating 50.00 ml of 0.01000 M HA with 0.01000 M NaOH to the fixed end-point pH of 9.80?

To reach the equivalence point, 50.00 ml of 0.01000 M NaOH are required. The equivalence-point volume is 100.00 ml, and the NaA concentration is 0.00500 M . The salt hydrolyzes, and the composition of the solution at the equivalence point may be calculated from K_b for the base, A^- .



Let $[OH^-]$ be x M . Then $[HA]$ is also x M , and $[A^-]$ is $0.00500 - x$ M . Substituting these concentrations in the basic ionization-constant expression gives

$$x, \text{ or } [OH^-], \text{ or } [HA] = 2.24 \times 10^{-5} \text{ } M \quad (\text{Eq pt})$$

If the titration is carried to pH 9.80, or pOH 4.20, then $[OH^-]$ is 6.3×10^{-5} M , and the end point is therefore past the equivalence point. At this end point, the ionization-constant expression of A^- must still be satisfied. Let $[HA]$ be y . Then

$[A^-] = 0.00500 - y$. Substituting these concentrations into the ionization-constant expression gives

$$\frac{y(6.3 \times 10^{-5})}{0.00500 - y} = \frac{1.01 \times 10^{-14}}{1.00 \times 10^{-7}}$$

$$y, \text{ or } [HA] = 0.80 \times 10^{-5} M \quad (\text{End pt})$$

At the end point, the excess of OH^- over HA is $6.3 \times 10^{-5} - 0.80 \times 10^{-5}$, or $5.5 \times 10^{-5} M$. The titration error is the volume of $0.01000 M$ $NaOH$ required to build up this excess in 100 ml of solution, or $5.5 \times 10^{-5} \times 100/0.01000$, or 0.55 ml. Since the correct equivalence-point volume is 50.00 ml, the relative end-point error is 1.10%.

TECHNIQUES FOR IMPROVING THE ACCURACY OF ACID-BASE TITRATIONS

(See Sec. 18C.4, p. 360)

Many methods have been devised for increasing the accuracy with which very weak (or dilute) acids and bases may be titrated. The following four methods are not of equal importance. They are chosen to illustrate the variety of ways in which accuracy may be improved.

Nonaqueous Titrations (F11)

The strengths (i.e., degree of ionization) of weak acids and bases may be greatly enhanced in appropriate solvents. Titrations in such media are widely used to improve the end-point sharpness in titrations of very weak acids and bases.

Titration of weak bases. In water, the strongest acid that may exist is H_3O^+ . Any very strong acid is quantitatively converted to H_3O^+ . Thus, all strong acids ($HClO_4$, HCl , HNO_3 , etc.) are diminished or *leveled* in strength in water, and no differences in strength can be detected among them.

However, there are solvents that are more acidic than water. For such solvents (i.e., glacial HAc), the protonated forms are stronger acids than H_3O^+ :



In glacial HAc , it is noted that $HClO_4$ is a stronger acid than HCl , which in turn is stronger than HNO_3 . In glacial HAc , therefore, $HClO_4$ is a stronger acid than in water, and reacts more completely with a given weak base.

Also, if a certain solvent is more acidic than water, a given base is more strongly ionized in the solvent than in water:



Thus, by titrating a given weak base in glacial HAc, not only is the strength of the base enhanced, but a stronger standard acid may be used to give a more complete reaction and a sharper end point than in water. Figure S18.2 shows titration curves for several bases so weak that their titrations in water are impossible. Bases that can be titrated to advantage in nonaqueous media are amines, amino acids, heterocyclic nitrogen compounds, alkaloids, and salts of weak acids. Some of these titrations are of considerable practical importance. In general, bases with pK_b values of 12 or less are quite accurately titratable in glacial HAc with HClO_4 as a titrant.

The performance of nonaqueous titrations is not much more difficult than aqueous ones. Acid-base indicators, the pH meter, or conductometric methods may be used to establish the end point. For the standardization of titrant HClO_4 , adequate and stable primary standards are available, such as KHP and diphenylguanidine.

Solvents of greater acidity than HAc have not been used much. There is of course a limit to how strong an acid may be used as a solvent.

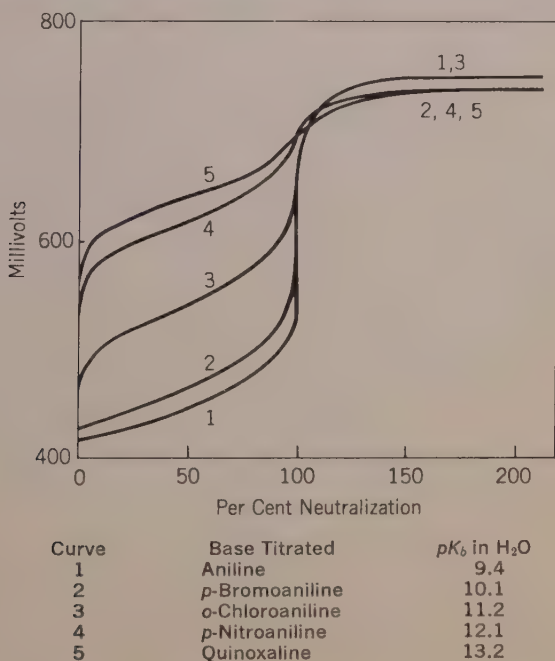


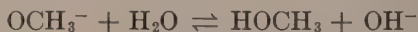
FIG. S18.2. Titration of Amines in Glacial Acetic Acid with 0.1 M HClO_4 . (Data taken from J. S. Fritz and G. S. Hammond, *Quantitative Organic Analysis* [New York: Wiley, 1957], Fig. 2, with permission of the publisher.)

If the solvent is too strong an acid, it competes against the standard acid for the weak base, and the steepness of the titration curve is reduced.

Acetic anhydride is used as a solvent to prevent the deleterious effect of small amounts of water that may be present in a sample (*vide infra*). Bases as weak as urea ($pK_b = 14$) are accurately titratable in acetic anhydride. Inert solvents (benzene, etc.) are sometimes admixed with HAc to increase the solubility of the sample or of the titration products.

There are a few circumventable practical difficulties in the performance of nonaqueous titrations. (1) Water in the system causes a diminution in sharpness of the end point. Small amounts of water are tolerable, but the tolerable amount decreases as the strength of the base being titrated decreases. (2) The color changes and transition ranges of indicators in nonaqueous solvents may be entirely different from their behavior in water. Values of pH obtained in a nonaqueous system cannot be easily related to values obtained in an aqueous system containing the same solutes. Little attempt has been made to correlate pH values in aqueous and nonaqueous systems as far as titrations are concerned, because to establish the end point, only changes in pH need to be noted.

Titration of weak acids. In water, the strongest base that can exist is OH^- . Any very strong base, like sodium methoxide ($NaOCH_3$), is quantitatively converted to OH^- .



As with strong acids, all very strong bases are leveled in strength, so that no differences may be detected among them. However, if a nonacidic solvent is used, the methoxide cannot undergo protonization; it survives and is more basic than it is in water, and it reacts more completely with a given weak acid to give a sharper end point than in water.

A variety of nonacidic solvents may be used, such as alcohols, or mixtures of alcohols with benzene, toluene, acetone, or dioxane. Glycol-hydrocarbon mixtures, dimethylformamide, and acetonitrile are also used.

A variety of basic titrants is also available. Alcoholic KOH is a stronger base than KOH in water, because alcohol is less acidic than water. $NaOCH_3$ in benzene-methanol is a good titrant, but tetraalkyl ammonium hydroxides are even better (*vide infra*). Sodium triphenylmethane is a very strong base, but it is readily destroyed by oxygen and is troublesome to use.

With a basic solvent, such as ethylenediamine, not only can strong bases be used as titrants, but a given acid is stronger (i.e., more ionized) than in water. Other basic solvents are butylamine and pyridine. An

advantage to the use of basic solvents is that they are better solvents for some organic acids than the nonacidic solvents described above. Solvents of greater basicity than ethylenediamine are not used; if the solvent is too strong a base, it competes with the titrant NaOCH_3 for the weak acid being titrated, and the sharpness of the end point is reduced.

End points may be established with acid-base indicators, the pH meter, or conductometric techniques. For the standardization of titrant NaOCH_3 or other strong bases, good primary standards are available, like benzoic acid.

Acidic substances that are determinable are carboxylic acids, amino acids, thiols, enols, imides, sulfonamides, barbiturates, phenols, and salts of weak bases.

Practical difficulties are similar to those encountered in titration of weak acids. (1) Only small amounts of water are tolerable, the amounts being smaller the weaker the base being titrated. Basic solvents and dimethylformamide avidly absorb CO_2 from air. For best precision, nonaqueous titrations with standard strong base are carried out under a stream of nitrogen. (2) Acid-base indicator behavior in nonaqueous solvents has been described on page 786. With a pH meter, glass electrode behavior is poor in the strongly basic solution when Na^+ or K^+ are present, but with tetraalkyl ammonium hydroxide titrants, the glass electrode gives good end points. (3) The Na and K salts formed in titrating some weak acids may precipitate in the nonacidic types of solvents (like benzene-methanol), causing coprecipitation errors. The solubilities of such salts may usually be increased by choice of more polar or more basic solvents. Precipitation of salts is not encountered with tetraalkyl ammonium hydroxide titrants.

The field of nonaqueous titrations is expanding rapidly, and the latest developments are subject to periodic review (S30).

Titration in Salt Media

The presence of a high salt concentration has a great effect on the ionization of HCl . Thus, the pH of $0.02\ M$ HCl in water is about 2, but the pH is around 0 in $0.02\ M$ HCl — $7\ M$ NaI .

In the titration of a weak base with standard HCl , the equivalence point comes in rather strongly acid solution, and the end-point inflection is poor because the addition of excess HCl past the equivalence point does not change the pH rapidly. In the presence of NaI , however, the ionization of HCl is enhanced, and a significant inflection is obtained in the titration of bases ($pK_b \leq 11$) too weak to titrate in water alone. Figure S18.3 compares the titrations of two weak bases in water and NaI media.

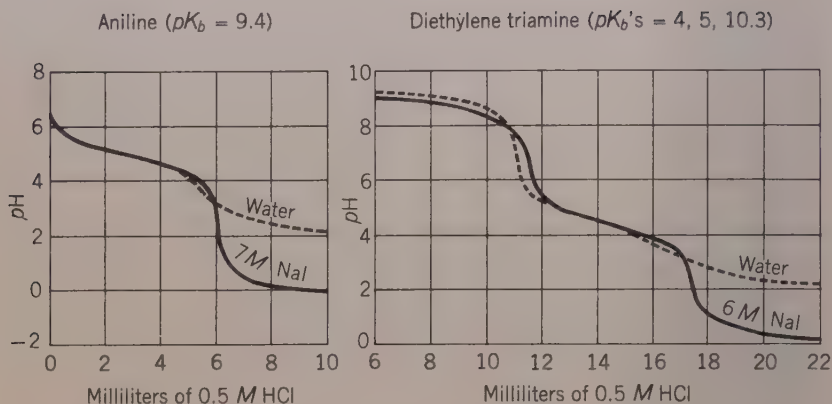
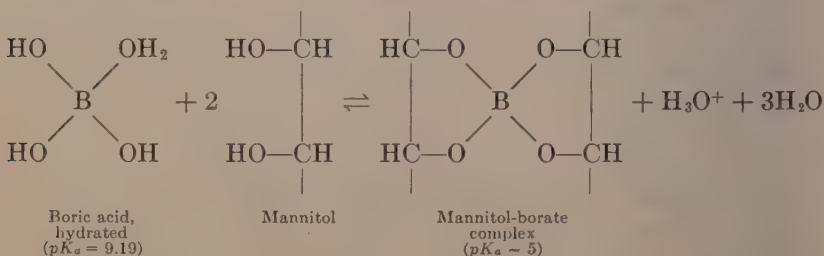


FIG. S18.3. Potentiometric Titration of Weak Bases in Water and Sodium Iodide Media (Reprinted from F. E. Critchfield and J. B. Johnson, *Analytical Chemistry*, 30, 1247 [1958], Figs. 1 and 4, by permission of the publisher.)

Complexation or Chemical Reaction

Chemical reactions may be used to enhance the strength of a weak acid, so that it will become more accurately titratable. An example is the complexation of boric acid (HBO_2 , $pK_a = 9.19$) with mannitol (a hexahydric alcohol, $\text{HOCH}_2 \cdot (\text{CHOH})_4 \cdot \text{CH}_2\text{OH}$) to form a complex having a pK_a around 5. In the presence of excess mannitol, the complex contains two moles of mannitol per mole of boron (S25). For a typical titration, the boric acid solution is made around half molar in mannitol. The complex forms rapidly, and is a strong enough acid to titrate accurately. Other polyhydric alcohols or hexoses can also be used.



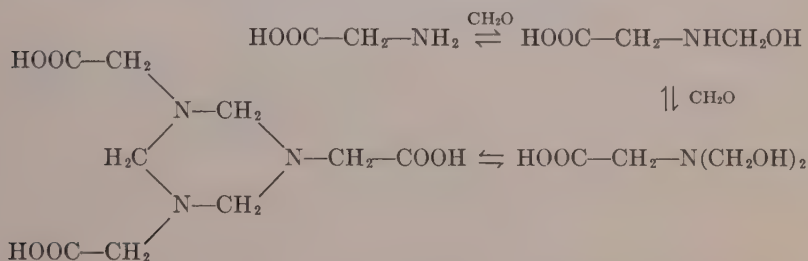
Another example may be found in the titration of amino acids. The amino acids are amphiprotic, but they are too weak to be accurately titratable with either standard acid or base. Thus, in glycine, the carboxylate proton ($pK_a \sim 10$) does not have nearly the acid strength that

it does in other carboxylic acids ($pK_a \sim 5$), because the proton is combined with the basic amino group:



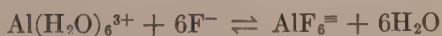
And, because the proton is associated with the amino group, the basic strength of the latter is not nearly so high as in other amine-type compounds.

In the presence of formaldehyde, however, the basic amino group is converted to less basic N-hydroxymethyl groups, and the acid strengths ($pK_a \sim 6$) of the resulting compounds more nearly resemble the strengths of carboxylic acids. The reactions (F9) seem to be

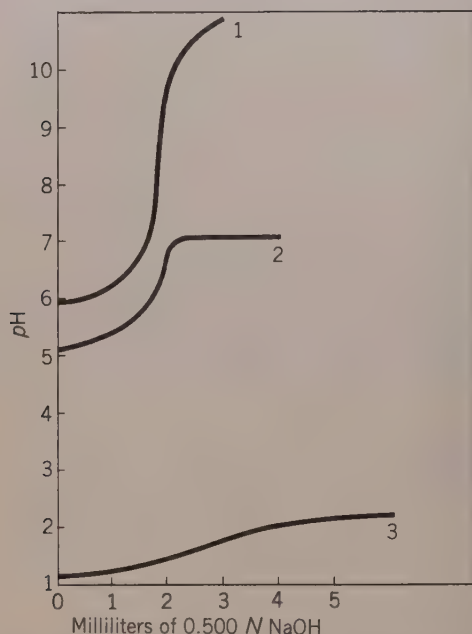


In summary, the weak amino acid is converted by formaldehyde to more strongly acid products that are more accurately titratable with standard base. Formaldehyde concentrations ranging from 6 to 16% are recommended by different investigators. With phenolphthalein as an indicator, titration errors appear to be only a few tenths of a per cent.

Sometimes an interference may be complexed to improve the end point of an acid-base titration. A rather common problem is to determine the free acid in a solution containing a hydrolyzable metal ion (i.e., one that is a fairly strong acid)—for example, an $\text{HNO}_3\text{-Al}(\text{NO}_3)_3$ solution. In attempting to titrate the HNO_3 with standard base, the Al^{3+} begins to hydrolyze (i.e., to react with standard base according to the equations on p. 769) before the HNO_3 equivalence point is reached, and the end point is poor. If, however, an excess of fluoride or oxalate is added, the Al^{3+} forms so stable a complex that the hydroxy complexes are not formed.



The titration of the HNO_3 in the presence of fluoride or oxalate then gives a sharp end point, as shown in Fig. S18.4. The principle is also useful in the determination of Al^{3+} by titration with standard base (W7).



1. 25-ml sample of 0.04 M HNO_3 -2 M $\text{Al}(\text{NO}_3)_3$ titrated in volume of 100 ml at 10-15°C after adding 30 g of $\text{KF} \cdot 2\text{H}_2\text{O}$.
2. As in 1, except 60 g of $\text{K}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ added instead of KF .
3. As in 1, except 50-ml sample used, and no KF .

FIG. S18.4. Titration of HNO_3 in $\text{Al}(\text{NO}_3)_3$ Solutions (Reprinted from W. J. Blaedel and J. J. Panos, *Analytical Chemistry*, 22, 910 [1950], Fig. 1, by permission of the publisher.)

Graphical Method

In the titration of a weak acid with standard strong base, the slope in the inflection region of the titration curve diminishes and the end point becomes poor as the strength or concentration of the weak acid decreases. Plotted differently, however, acid-base titration data permit accurate calculations for very dilute solutions of very weak acids and bases. The method of Gage (G1), given below, is one of several that are described in the chemical literature.

Instead of plotting $p\text{H}$ against volume of standard solution to give a conventional titration curve, functions of these quantities are plotted that result in a straight-line titration curve. The concentration and ionization constant of the weak acid or base may be evaluated from the slope and intercepts of the straight line.

At any instant in the titration system, let C_a be the stoichiometric

concentration of the weak acid being titrated, and let C_b be the stoichiometric concentration of added base. At each point in the titration, C_b is calculated from the volume and concentration of the added standard base and the volume of the titration system. C_a also changes as standard base is added. If the pH is measured at each point in the titration, then $[H_3O^+]$ may be calculated from the pH .

$$[H_3O^+] = \text{antilog} (-pH)$$

In the titration of very weak or very dilute acids, the ionization of water itself may be significant, and the general equation relating $[H_3O^+]$ to C_b throughout the titration is given by

$$\frac{[H_3O^+]}{K_a} = \frac{C_a - C_b - [H_3O^+] + [OH^-]}{C_b + [H_3O^+] - [OH^-]} \quad (Sa)^*$$

The quantities C_b , $[H_3O^+]$, and $[OH^-]$ are measurable or calculable, and the form of Eq. *Sa* is simplified by defining a composite variable,

$$x = C_b + [H_3O^+] - [OH^-] \quad (Sb)$$

$$\frac{[H_3O^+]}{K_a} = \frac{C_a - x}{x} \quad (Sc)$$

Equation *Sc* may be rearranged to give

$$\frac{[H_3O^+]x}{K_a} + x = C_a \quad (Sd)$$

A plot of $x[H_3O^+]$ as ordinates against x as abscissae gives a straight line of slope $-K_a$. If the data are extrapolated to intercept the axes, the vertical intercept is $K_a C_a$, and the horizontal intercept is C_a . The slope and intercepts thus permit calculation of C_a (and K_a , if desired).

Figure S18.5 gives data for the titration of a dilute solution of an acid so weak that no inflection is obtained in the conventional plot of pH against volume of standard base. A plot of $x[H_3O^+]$ against x yields a straight line. It is left as an exercise for the student to calculate K_a and C_a from the slope and intercepts.†

*An equation practically identical to this equation has been derived in detail (Eq. *h*, p. 774).

†It is advantageous to use a microburet, and to titrate with a standard base solution that is much more concentrated than the weak acid solution being titrated. Then, the volume of standard base is small, and the volume of the solution being titrated does not change much. Then C_a remains practically constant throughout the titration, which simplifies calculations. This condition is met quite well in Fig. S18.5.

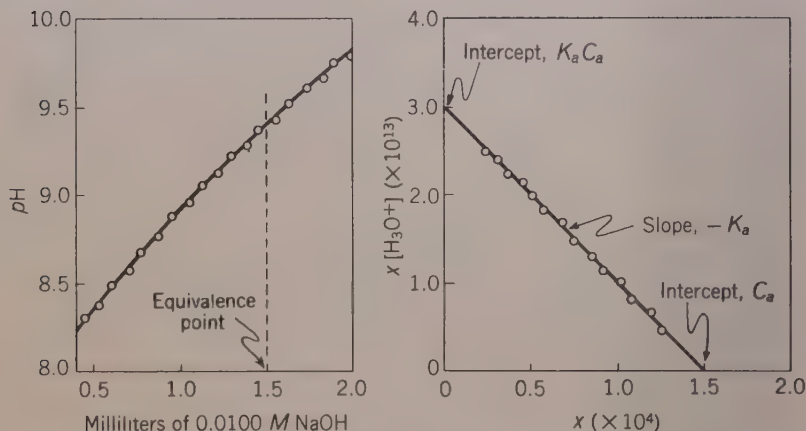


FIG. S18.5. Titration of Weak Acids—Conditions: calculated for the titration of 100.0 ml of $1.50 \times 10^{-4} M$ HA ($pK_a = 8.70$) with 0.0100 M NaOH.

A simple extension of the equations permits handling data for mixtures of weak acids or polyprotic acids. A particular advantage of the method is that data in the buffer region (where $pH = pK_a$) weigh most heavily in determining the straight line. As a consequence, it is possible to resolve acids whose pK_a 's are too close together to permit resolution by the conventional method. A disadvantage is the time and effort required for calculations and graphing.

This graphical procedure nicely supplements titration in nonaqueous solutions, for it is applicable to samples that happen to be in aqueous solution, and whose transfer to nonaqueous medium might be difficult.

The technique has been applied to the determination of weak acids and bases ($pK \sim 9$) at concentrations around $10^{-4} M$, with relative errors of only a few per cent. Of course, some experimental precautions must be exercised that are not encountered in ordinary titrations. For instance, the dilute solutions necessitate stringent exclusion of air; otherwise the carbonate error becomes serious. Also, pH values must be read more precisely than in titration to an inflection point.

RIGOROUS CALCULATION OF POINTS ON POLYPROTIC ACID TITRATION CURVES

(See Sec. 18D.1, p. 361)

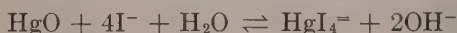
Example. Calculate $[\text{H}_3\text{O}^+]$ when 51.00 ml of NaOH are added in the titration of H_2P under the conditions of Fig. 18.9 (p. 362).

The composition of the solution may be calculated as follows: The millimoles of NaOH added are $(0.1000)(51.00)$, or 5.100. The millimoles of H_2P present are

mary standard substances which are all decomposed quantitatively to the carbonates on proper heating. They offer little advantage over Na_2CO_3 itself.

Tris (hydroxymethyl) aminomethane $((\text{HO}\cdot\text{CH}_2)_3\text{C}\cdot\text{NH}_2, pK_b = 5.90)$ is commercially available in high purity. It can be easily dried at 105°C to give a nonhygroscopic preparation (**K19**).

HgO has a high equivalent weight and is stable. As a primary standard for HCl solutions it may be dissolved in a concentrated solution of KI , whereupon an equivalent amount of KOH is liberated. The KOH is titrated with the acid to a phenolphthalein end point.



KIO_3 is an excellent primary standard (p. 845).

Standards for NaOH and other strong base solutions. Benzoic acid ($\text{C}_6\text{H}_5\cdot\text{COOH}$) is an excellent primary standard. It permits the same accuracy as KHP , but is more troublesome to prepare.

Oxalic acid ($\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O}$) is very stable over quite a range of normal atmospheric conditions, but some pains are required to obtain samples with precisely the proper amount of water. Oxalic acid must be titrated as a dibasic acid with phenolphthalein as an indicator.

Sulfamic acid ($\text{HSO}_3\cdot\text{NH}_2$) is a strong monobasic acid which may be used to standardize NaOH solutions either to the methyl orange or to the phenolphthalein end points. It is sufficiently stable to dry at 100 – 105°C , and the product is not hygroscopic. The dry solid is stable, but hydrolysis occurs in the presence of moisture.



This reaction is not sufficiently rapid to interfere in an ordinary titration, but it does cause trouble under certain circumstances. If this reaction occurs after the sample is weighed out, there is no stoichiometrical error produced by the decomposition, since one mole of titratable bisulfate is produced per mole of sulfamic acid decomposed. However, the ammonium ion produced at the same time has a buffering effect, and destroys the sharpness of the phenolphthalein end point. This effect is noticeable if the solutions are heated or allowed to stand for a long time before titration. If the hydrolysis occurs before the samples are weighed out (as may be the case if rather wet samples are dried at elevated temperatures) there is additional error, for the equivalent weight of NH_4HSO_4 is not the same as that of the sulfamic acid.

Monosodium diglycolate ($\text{HOOC}\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{COONa}$) is easily recrystallized and may be dried at 120°C . It is a stronger acid than KHP , and gives a sharper end point with phenolphthalein as indicator (**K3**).

HCl solutions of very accurately known composition may be prepared

by distillation. In general, when mixtures are distilled, the composition of the vapor is different from that of the boiler contents; this is the principle on which separation by distillation is based. However, some substances form *azeotropic* mixtures, which do not change in composition when distilled (D1). HCl forms an azeotropic mixture with water at about 20% by weight of HCl, or about 6 M HCl. If a solution containing more (or less) HCl than this is distilled, the first portions of the distillate are relatively richer (or poorer) in HCl than the boiler contents, which therefore approach the azeotropic composition. In practice, the first portions of distillate are rejected until the distillate that comes over has the azeotropic composition. The HCl content of the azeotropic solution is very accurately known as a function of the pressure under which distillation occurs, and such solutions may be used to prepare standard HCl solutions by proper dilution (F6).

Absolute H_2SO_4 may also be prepared as a primary standard, with composition accurately known to within a few hundredths of a per cent. Purification may be achieved either by azeotropic distillation or by freezing (K21).

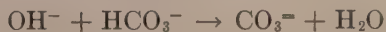
TITRATION OF CARBONATE MIXTURES AND PHOSPHATE MIXTURES

Analysis of $\text{NaOH-Na}_2\text{CO}_3\text{-NaHCO}_3$ Mixtures

(See Sec. 18D.2, p. 363)

If a solution contains only Na_2CO_3 , it may be titrated with standard acid, first to the phenolphthalein end point (pH 9–10), and then further to the methyl orange end point (pH 4–5), as shown in Fig. 18.9 (p. 362). Titration of the sample to two end points thus gives two determinations (checks) on the amount of Na_2CO_3 . If a solution contains NaOH or NaHCO_3 in addition to Na_2CO_3 , titration to the phenolphthalein and methyl orange end points allows estimates of both components, as shown by the following considerations.

Suppose that a solution is prepared by dissolving various amounts of any or all of the following substances: NaOH, Na_2CO_3 , and NaHCO_3 . Compositions of all of the possible solutions that could result are (a) NaOH, (b) Na_2CO_3 , (c) NaHCO_3 , (d) $\text{NaOH-Na}_2\text{CO}_3$, (e) $\text{Na}_2\text{CO}_3\text{-NaHCO}_3$. Mixtures of NaOH and NaHCO_3 are not stable, but react,



giving simple mixtures of the types b, d, or e, depending on whether the amount of NaOH is equal to, greater than, or less than the NaHCO_3 . Thus the compositions of all aqueous systems containing NaOH, Na_2CO_3 , and NaHCO_3 may be expressed as one of the five types above, containing at most only two solutes.

The composition of the sample may be qualitatively deduced from the relative volumes of standard acid required to titrate a given-sized sample to the phenolphthalein and methyl orange end points. Thus if more than twice as much standard acid is required to reach the methyl orange end point as is required to reach the phenolphthalein end point, the sample must contain NaHCO_3 as well as Na_2CO_3 . Similar reasoning for the other types of mixtures leads to the conclusions summarized in Table S18.1.

TABLE S18.1
TITRATION OF NaOH - Na_2CO_3 - NaHCO_3 MIXTURES

Mixture	Relationship between A_m and A_p *
NaOH	$A_m = A_p$
Na_2CO_3	$A_m = 2A_p$
NaHCO_3	$A_m > A_p = 0$
NaOH - Na_2CO_3	$A_m < 2A_p$
Na_2CO_3 - NaHCO_3	$A_m > 2A_p$

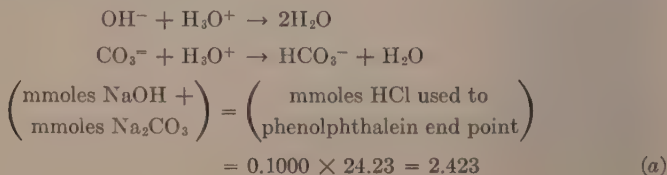
* A_m and A_p are the volumes of standard acid required to reach the methyl orange and phenolphthalein end points, respectively.

After this qualitative estimate of sample composition, the concentrations of the components may be calculated from the end-point volumes as in the following example.

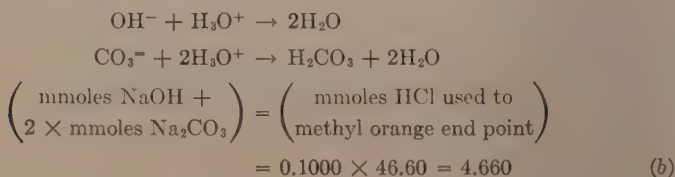
Example. A 25.00-ml aliquot of a solution containing NaOH and/or Na_2CO_3 and/or NaHCO_3 requires 24.23 ml of 0.1000 N HCl to the phenolphthalein end point and an additional 22.37 ml from the phenolphthalein to the methyl orange end point. Assuming that end-point errors are negligible, calculate the composition of the sample.

Since A_m (24.23 + 22.37, or 46.60 ml) is less than twice A_p (24.23 ml), the sample must contain NaOH as well as Na_2CO_3 .

To the phenolphthalein end point:



To the methyl orange end point:



From the difference between Eqs. *a* and *b*, the number of mmoles of Na_2CO_3 in the 25-ml aliquot is $4.660 - 2.423$, or 2.237 . The Na_2CO_3 concentration is therefore $2.237/25.00$, or $0.0895\text{ }M$.

By difference, the number of mmoles NaOH in the 25-ml aliquot is $2.423 - 2.237$, or 0.186 . The NaOH concentration is therefore $0.186/25.00$, or $0.00744\text{ }M$.

Analysis of Phosphate Mixtures

(See Sec. 18D.2, p. 363, and Exp. 18.5, p. 376)

Suppose that a solution is prepared by dissolving any or all of the following substances in water: HCl , H_3PO_4 , NaH_2PO_4 , Na_2HPO_4 , Na_3PO_4 , NaOH . In general, reaction occurs, and the composition of the resulting solution may be simply expressed in terms of at most two adjacent substances in the series, plus NaCl , as shown in the following two examples.

Example S1. Suppose that there are added to the same solution 3.43 moles of HCl , 0.61 mole of H_3PO_4 , 1.06 moles of NaH_2PO_4 , 3.94 moles of Na_3PO_4 , and 1.33 moles of NaOH . Express the molar composition of the resulting solution as simply as possible.

First, perform the hypothetical process of removing all ionizable H^+ , and then recombine this H^+ with the bases in solution. The strongest base reacts first, and then the weaker bases combine successively with H^+ until it is all consumed.

The total moles of ionizable H^+ are

$$3.43 + 3(0.61) + 2(1.06) = 7.38$$

\uparrow
From
 HCl

\uparrow
From
 H_3PO_4

\uparrow
From
 NaH_2PO_4

The total moles of $\text{PO}_4^{=}$ are $0.61 + 1.06 + 3.94$, or 5.61 .

The total moles of OH^- are 1.33 , from the NaOH .

First, 1.33 moles of H^+ react with the 1.33 moles of OH^- , leaving $7.38 - 1.33 = 6.05$ moles of H^+ .

Per mole of total $\text{PO}_4^{=}$, there are $6.05/5.61 = 1.1$ moles of H^+ , so that the total phosphate exists as a mixture of $\text{HPO}_4^{=}$ and H_2PO_4^- . Therefore 5.61 moles of $\text{PO}_4^{=}$ react with 5.61 moles of H^+ to form 5.61 moles of $\text{HPO}_4^{=}$, leaving $6.05 - 5.61 = 0.44$ mole of H^+ .

The 0.44 mole of H^+ reacts further with 0.44 mole of $\text{HPO}_4^{=}$ to form 0.44 mole of H_2PO_4^- , leaving $5.61 - 0.44 = 5.17$ moles of $\text{HPO}_4^{=}$.

The resulting solution may therefore be considered to be an Na_2HPO_4 - NaH_2PO_4 - NaCl mixture containing 5.17 moles of Na_2HPO_4 , 0.44 mole of NaH_2PO_4 , and 3.43 moles of NaCl . (The NaCl is obtained from the HCl .)

The answers may be checked by performing a material balance on Na^+ . The total Na^+ added is

$$1.06 + 3(3.94) + 1.33 = 14.21 \text{ moles}$$

\uparrow
From
 NaH_2PO_4

\uparrow
From
 Na_3PO_4

\uparrow
From NaOH

The total Na^+ in the final solution is

$$\begin{array}{c}
 3.43 + 2(5.17) + 0.44 = 14.21 \text{ moles} \\
 \begin{array}{ccc}
 \uparrow & \uparrow & \uparrow \\
 \text{From} & & \text{From } \text{NaH}_2\text{PO}_4 \\
 \text{NaCl} & \text{From } \text{Na}_2\text{HPO}_4 &
 \end{array}
 \end{array}$$

Example S2. A 28.0-ml portion of 0.265 M H_3PO_4 is mixed with 34.0 ml of 0.290 M Na_2HPO_4 . Assuming that volumes are additive, express the composition of the resulting solution.

$$\text{mmoles } \text{H}_3\text{PO}_4 = 28.0 \times 0.265 = 7.43$$

$$\text{mmoles } \text{Na}_2\text{HPO}_4 = 34.0 \times 0.290 = 9.86$$

$$\text{Total mmoles of ionizable } \text{H}^+ = 3(7.43) + 9.86 = 32.15$$

$$\text{Total mmoles of } \text{PO}_4^{3-} = 7.43 + 9.86 = 17.29$$

Since there are between one and two moles of H^+ per mole of PO_4^{3-} , the phosphate may be assumed to exist as a mixture of HPO_4^{2-} and H_2PO_4^- . Therefore 17.29 mmoles of PO_4^{3-} combine with 17.29 mmoles of H^+ to form 17.29 mmoles of HPO_4^{2-} , leaving $32.15 - 17.29 = 14.86$ mmoles of H^+ .

And 14.86 mmoles of H^+ combine further with 14.86 mmoles of HPO_4^{2-} to form 14.86 mmoles of H_2PO_4^- , leaving $17.29 - 14.86 = 2.43$ mmoles of HPO_4^{2-} .

The solution therefore contains 2.43 mmoles of Na_2HPO_4 and 14.86 mmoles of NaH_2PO_4 , in a volume of $28.0 + 34.0 = 62.0$ ml. The concentration of Na_2HPO_4 is therefore $2.43/62.0 = 0.0392 M$, and the concentration of NaH_2PO_4 is $14.86/62.0 = 0.2397 M$.

As a check, a material balance should be made on Na^+ . The millimoles of Na^+ put into the solution as Na_2HPO_4 are 2×9.86 , or 19.72. The millimoles of Na^+ in the final solution are 14.86 (from NaH_2PO_4) + 2×2.43 (from Na_2HPO_4), or 19.72.

From the examples above, the compositions of all $\text{HCl-H}_3\text{PO}_4\text{-NaH}_2\text{PO}_4\text{-Na}_2\text{HPO}_4\text{-Na}_3\text{PO}_4\text{-NaOH}$ mixtures may be found and expressed as one of the eleven types shown in Table S18.2. (NaCl may also be present, but, for analytical purposes, this is regarded as an inert material, since it is not titratable with standard acid or base.)

Depending on the relative equivalents of standard acid and/or base required to titrate a particular sample to the methyl orange and phenolphthalein end points, the sample may be qualitatively identified as one of the mixtures shown in Table S18.2. For example, if a sample is a mixture of HCl and H_3PO_4 , the equivalents of standard base required to reach the phenolphthalein end point are less than twice the equivalents required to reach the methyl orange end point. Similar reasoning for the other types of mixtures leads to the conclusions summarized in the table.

After the sample is identified as one of the types above, the concentrations of the components may be calculated from the titration data, as shown in the following example.

TABLE S18.2
TITRATION OF PHOSPHATE MIXTURES

MIXTURE	RELATIONSHIPS AMONG B_m , B_p , A_m , A_p *	
	Titration with Base	Titration with Acid
HCl.....	$B_p = B_m > 0$	
H_3PO_4	$B_p = 2B_m > 0$	
NaH_2PO_4	$B_p > B_m = 0$	$A_m = 0$
Na_2HPO_4	$B_p = 0$	$A_m > A_p = 0$
Na_3PO_4		$A_m = 2A_p > 0$
NaOH.....		$A_m = A_p > 0$
HCl- H_3PO_4	$0 < B_p < 2B_m$	
H_3PO_4 - NaH_2PO_4	$B_p > 2B_m > 0$	
NaH_2PO_4 - Na_2HPO_4	$B_p > B_m = 0$	$A_m > A_p = 0$
Na_2HPO_4 - Na_3PO_4		$A_m > 2A_p > 0$
Na_3PO_4 -NaOH.....		$0 < A_m < 2A_p$

* B_m and B_p are the equivalents of standard base required to titrate the sample to the methyl orange and phenolphthalein end points, respectively. A_m and A_p are the equivalents of standard acid required to titrate the sample to the methyl orange and phenolphthalein end points, respectively.

Example S3. A 25.00-ml portion of a phosphate mixture requires 10.87 ml of 0.1000 *N* base for titration to the methyl orange end point. Another 25.00-ml portion of the mixture requires 46.43 ml of the base for titration to the phenolphthalein end point. Give the composition of the sample.

Since more than twice as much base is required for the phenolphthalein end point, the sample must contain NaH_2PO_4 as well as H_3PO_4 .

$$\begin{aligned} \left(\text{mmoles } H_3PO_4 \right) &= \left(\begin{array}{c} \text{meq of base to the} \\ \text{methyl orange end point} \end{array} \right) \\ &= 0.1000 \times 10.87 = 1.087 \end{aligned} \quad (a)$$

$$\begin{aligned} \left(\begin{array}{c} 2 \times \text{mmoles } H_3PO_4 \\ + \text{mmoles } NaH_2PO_4 \end{array} \right) &= \left(\begin{array}{c} \text{meq of base to the} \\ \text{phenolphthalein end point} \end{array} \right) \\ &= 0.1000 \times 46.43 = 4.643 \end{aligned} \quad (b)$$

From Eqs. *a* and *b*, the millimoles of NaH_2PO_4 in the sample are $4.643 - 2(1.087) = 2.469$.

The concentration of H_3PO_4 in the sample is therefore $1.087/25.00 = 0.04348 M$, and the concentration of NaH_2PO_4 is $2.469/25.00 = 0.0988 M$.

PREPARATION OF STUDENT UNKNOWN SAMPLES

(See Exps. 18.2–18.6, pp. 370–85)

Na_2CO_3 - $NaCl$ samples are recommended for Exp. 18.2, KHP-KCl for 18.3, and $(NH_4)_2SO_4$ - Na_2SO_4 for Exp. 18.6. Different samples in a set should not be highly dissimilar in composition: 80–100% of Na_2CO_3 , KHP, or $(NH_4)_2SO_4$ is a suitable range. These solid sample mixtures

may be prepared from reagent-grade chemicals, as described on page 694. Na_2CO_3 in large batches should be dried at 250°C before being weighed out. NaCl , KCl , and Na_2SO_4 may be dried at 150°C . KHP and $(\text{NH}_4)_2\text{SO}_4$ need be dried for only a few hours at 100°C .

For Exp. 18.4, a stock solution of $0.50\text{ }M\text{ H}_3\text{PO}_4$ (34.0 ml conc. H_3PO_4 per liter of solution) is prepared. Carefully measured portions ranging from 35 to 45 ml should be given to each student, so that, when diluted to 250 ml, a 50-ml aliquot will require 35–45 ml of $0.10\text{ }N$ base for titration. An automatic zero buret with a two-way stopcock is useful for dispensing. If the solution is issued by a person other than the instructor, careful instruction should be given to prevent error in both withdrawal and record keeping.

It is recommended that the H_3PO_4 stock solution be carefully analyzed by the instructor, and that all student results be graded with reference to the instructor's value as the correct one. The practice of determining a "most probable concentration" for the stock solution by accumulating and averaging student results should be avoided for several reasons. (1) There is no check upon errors beyond the student's control. (2) The "most probable concentration" may be biased by errors made by the average student, and the very careful worker who does not make these errors may be penalized. (3) There may be a considerable lag between the submission and the grading of reports, especially of those that are handed in early. This is undesirable not only for the student but also from the standpoint of controlling and revealing errors.

The $0.50\text{ }M\text{ H}_3\text{PO}_4$ stock solution of Exp. 18.4 may also be used for Exp. 18.5. The HCl may be issued in the form of a $0.50\text{ }M$ stock solution (40 ml conc. HCl per liter of solution). Each student should be given 17–23 ml each of the H_3PO_4 and the HCl solutions, so that, when diluted to 250 ml, a 50-ml aliquot will require 35–45 ml of $0.10\text{ }N$ base for titration to the pH 4–5 end point, and about 20 ml more to the pH 9–10 end point.

The unknowns are kept within rather narrow limits to facilitate the writing of experimental directions and the grading of results. If it is felt that such unknowns do not sufficiently exercise the ingenuity of the student, more varied samples may be issued.

SUPPLEMENTARY QUESTIONS

Section 18A

S1. If activity coefficients were employed in the calculations, explain qualitatively how the curves of Fig. 18.2 (p. 345) would be altered.

S2. In calculating a point on a titration curve, the usual procedure is to calculate the pH corresponding to the addition of a particular volume of titrant. Explain why

it would be much easier to calculate the volume of titrant corresponding to a particular pH .

Section 18B

S1. In the structural formulae on page 779, describe specifically the changes in bonding that account for the differences in color between the acid and base forms of each indicator.

S2. Suppose that the transition pH for a particular indicator is temperature invariant. How does the transition pOH depend on temperature?

S3. Formulate a mixed indicator with bromophenol blue that will be gray around pH 4.

S4. At about what pH will a mixture of bromothymol blue and phenol red be gray?

S5. Explain the behavior if a mixed indicator like bromocresol green–methyl red is prepared with too high a proportion of bromocresol green.

S6. Consider how the pH changes as a solution of $BaCl_2$ is titrated with $0.1 M Na_2CO_3$. Select an acid-base indicator to indicate the equivalence point. The limitations of this method have been discussed (W14).

S7. Describe in detail how to determine the end point conductometrically in the titration of HCl with $NaOH$. Draw a rough titration curve.

Section 18C

S1. A mixture consists of aniline and its hydrochloride in an inert solvent. Outline how the amount of aniline and the amount of aniline hydrochloride might be determined.

S2. Repeat Ques. S1 for an HAc - $NaAc$ mixture.

S3. Explain the nature of the interference of water in a nonaqueous titration. Explain why water interferes in a nonaqueous titration when anhydrous HAc is used as a solvent, but not when HAc -acetic anhydride is used as a solvent.

S4. A sample containing methylamine and aniline cannot be titrated with standard HCl to a good double end point in either water or HAc , but it can be so titrated in a neutral solvent like chloroform or acetonitrile. Explain.

S5. Explain why a mixture of phenol, HAc , and HCl can be titrated to a good triple end point with tetrabutyl ammonium hydroxide in methyl ethyl ketone, but not in water (H4).

S6. Speculate on the mechanism by which the ionization of HCl is enhanced in a concentrated NaI solution.

Experiments

S1. A portion of sulfamic acid is accurately weighed out for standardizing an $NaOH$ solution, but some decomposition to NH_4HSO_4 occurs before titration. Describe the error if the titration is carried out to (a) the phenolphthalein end point, (b) the methyl orange end point.

S2. Write the balanced equation for the thermal decomposition of $KHC_4H_4O_6$ to K_2CO_3 .

SUPPLEMENTARY PROBLEMS

Section 18A

S1. On the titration curve of Fig. 18.3 (p. 345), for $K_a = 10^{-7}$, check the pH values when the following volumes of $NaOH$ are added: 49.50, 50.00, 50.10 ml.

S2. On the titration curve of Fig. 18.5 (p. 349), for $K_b = 10^{-7}$, check the pH values when the following volumes of HCl are added: 49.90, 50.00, 50.10 ml.

S3. Find an expression for the slope of the titration curve ($d(pH)/dC_b$) beyond the equivalence point for the titration of the monoprotic acid HA with standard $NaOH$. Assume that the basic ionization of the base A^- is the predominant equilibrium. Let: C_a be the concentration of NaA , assumed constant around the equivalence point; C_b be the concentration of excess $NaOH$; and K_b be the ionization constant for the base A^- . Evaluate the slope at the equivalence point, $C_b = 0$.

$$Ans. \quad 0.4343/\sqrt{C_b^2 + 4K_bC_a}; \quad 0.4343/\sqrt{4K_bC_a}.$$

S4. Activity effects are neglected in the titration curves of Fig. 18.2. For $K_a = 10^{-5}$, calculate the pH at the beginning of the titration, at the halfway point, and at the equivalence point, correcting for activity effects. Plot the three corrected points lightly on Fig. 18.2, and compare with the uncorrected curve. (Assume that the activity coefficient of A^- is the same as that of acetate.)

Section 18B

S1. From data in Appendix VIII, speculate on the nature of the ionization of thymol blue.

Ans. Diprotic acid; H_2In , red; HIn^- , yellow;

In^{2-} , blue; $pK_1 = 2.0$; $pK_2 = 8.8$.

S2. Suppose that for a simple diprotic acid indicator, the colors of H_2In , HIn^- , and In^{2-} are orange, blue, and violet, respectively. Suppose further that K_1 is only a few times (say fivefold) greater than K_2 . Describe the magnitude and location of the transition range.

S3. Derive an expression showing how $p\alpha_H$ at the center of the transition range for the indicator HIn depends upon ionic strength (μ). Assume that the ionic activity coefficients are given by the Debye-Huckel limiting law (Prob. S8, p. 714).

Ans. $pK_1 - 0.5\sqrt{\mu}$.

S4. (a) Consider qualitatively how the pH changes during the titration of 50.00 ml of a solution containing 0.1000 M $BaCl_2$ and $1.0 \times 10^{-4} M$ HCl with standard 0.1000 M K_2CrO_4 ($\kappa 19$, Vol. I, pp. 63–66).

(b) Considering that only the $BaCrO_4$ solubility-product equilibrium and the acid ionization of $HCrO_4^-$ are important, calculate the pH at 49.00, 49.50, 50.00, 50.50, and 51.00 ml of added K_2CrO_4 .

Ans. 5.22 (at 50.00 ml).

(c) For any of the points in part b, show that formation of $Cr_2O_7^{2-}$ is negligible.

(d) In the light of answers to part b, choose a method for selecting the equivalence point in the titration of an unknown sample of $BaCl_2$.

(e) Speculate on the disadvantages of this titration procedure.

(f) Could this procedure be applied to the titration of $SrCl_2$?

Section 18C

S1. Calculate the error involved in titrating 50.00 ml of 0.03000 M HA ($K_a = 1.00 \times 10^{-7}$) with 0.03000 M $NaOH$ to a fixed end-point pH of 9.80. Compare the answer with the example on page 783.

Ans. 0.13 ml, or 0.26%.

S2. Compute and plot points to define the curve for the titration of 50.00 ml of a solution containing 0.0990 M $NaOH$ and 0.0010 M Na_2CO_3 with 0.1000 M HCl , in the pH range 4–10. Assume that no CO_2 is lost. Using this curve, discuss the error caused by carbonate in a standard base when unknown acid solutions are being titrated.

S3. A 100-ml portion of a weak monoprotic acid is titrated with standard 0.0100 M $NaOH$. The following pairs of figures give both the milliliters of standard solution

and pH at various points in the titration: 0.053—7.71, 0.100—8.00, 0.124—8.10, 0.160—8.22, 0.225—8.40, 0.283—8.52, 0.383—8.70, 0.600—9.00, 0.681—9.11, 0.792—9.22, 0.964—9.39, 1.102—9.52, 1.333—9.70, 1.910—9.99.

(a) Plot a conventional titration curve, to show that it has no perceptible inflection. (b) From a plot of $x[\text{H}_3\text{O}^+]$ against x , calculate K_a and the concentration of the weak acid by Gage's method. (Note that the volume of standard NaOH required is so small compared to the volume of titrated solution that C_a may be considered constant throughout the titration.) *Ans.* $K_a = 1.00 \times 10^{-9}$; $C_a = 1.00 \times 10^{-4} M$.

S4. Consider the error that results from ignoring activity effects in Gage's method. Assume that the whole titration takes place at constant ionic strength.

S5. A solution contains 0.100 M HX ($pK_a = 4.00$) and 0.100 M HY ($pK_a = 6.00$). Calculate the percentage of HY that is neutralized when the NaOH added is just equivalent to (a) half of the HX, (b) all of the HX. Explain how the answers support the statement that Gage's method resolves a weak acid mixture better than does the conventional method. *Ans.* (a) 1.0%; (b) 9%.

S6. In the titration of a weak base (B) with a standard strong acid, a trace of a visual weak base indicator (In^-) is added. The indicator is a weaker base than B. After the equivalence point, B is quantitatively neutralized, and $[\text{H}_3\text{O}^+]$ increases proportionally to the excess of standard acid added. Show that the indicator ratio, $[\text{HIn}]/[\text{In}^-]$, is proportional to $[\text{H}_3\text{O}^+]$, and therefore to the volume of standard acid. A plot of $[\text{HIn}]/[\text{In}^-]$ (determinable spectrophotometrically) against volume of standard acid therefore gives a straight line which extrapolates back to the equivalence-point volume of standard acid. This procedure, like that of Gage, is suitable for the titration of acids and bases ($pK \sim 9$) too weak to give good inflection points in conventional titrations (R3). Pyridine, aniline, and acetates are accurately titratable with standard acid.

Section 18D

S1. Verify the pH values in the titration of H_2P under the conditions of Fig. 18.9 (p. 362), after the following volumes of NaOH are added: 0.00, 30.00, 49.00, 50.00, 50.10, 70.00, 99.90, 100.00 ml.

S2. Verify the pH values in the titration of H_2SO_4 under the conditions of Fig. 18.9, after the following volumes of NaOH are added: 0.00, 50.00, 99.90, 100.00, 101.00 ml.

Experiments

S1. What should be the sample size, in order that each milliliter of 0.1000 N HCl used in titrating an Na_2CO_3 -NaCl sample to a methyl orange end point should be equivalent to one per cent of Na_2CO_3 in the sample? *Ans.* 0.5300 g.

S2. A 0.6200-g portion of HgO is used as a primary standard for standardizing an HCl solution. What is the normality of the HCl solution if 36.92 ml are required for titration?

S3. A 0.4000-g portion of KIO_3 is used as a primary standard for standardizing an HCl solution. What is the normality of the HCl solution if 49.23 ml are required for titration? *Ans.* 0.2278 N .

S4. Verify the pH values on the curve of Fig. 18.10 (p. 369) when the following volumes of HCl are added: 39.50, 39.80, 40.00, 40.10, 41.50 ml.

S5. Verify the pH values on the curve of Fig. 18.12 (p. 375) when the following volumes of NaOH are added: 49.50, 49.80, 50.00, 50.10, 51.00 ml.

S6. Explain why the following method of titrating an HCl - H_3PO_4 mixture might be more effective than the procedure of Exp. 18.5 in reducing the carbonate error. Out-

line the method for calculating the HCl and H_3PO_4 contents of the sample. (a) Titrate the sample with standard base to the pH 4–5 end point, going only far enough past to establish it with certainty. Let V_1 be the volume of base required to reach the first end point. (b) Add a small, unmeasured volume of 0.1 N HCl, sufficient to bring the mixture back to the acid side of the first end point. The excess of acid should be kept small, less than 0.5 ml. Boil gently to remove CO_2 . Cool. (c) Refill the base buret to the zero mark and titrate the mixture, establishing both inflection points precisely. Let V_{12} be the volume of standard base required to pass from the first to the second end point. Let N_1 and N_2 be the base normalities to the pH 4–5 and pH 9–10 end points, respectively.

S7. Calculate the equivalence-point pH in the titration of 0.100 M tris (hydroxymethyl) aminomethane with 0.100 M HCl, and explain why a sharper end point is obtained than with Na_2CO_3 . *Ans.* 4.70; tris is a monoequivalent base.

S8. A certain solution is 0.0500 M in each of the following: Na_2PO_4 , NaHCO_3 , and Na_2CO_3 . How many ml of 0.100 N HCl will be required to titrate 20.0-ml portions of the solutions to: (a) the methyl orange end point, (b) the phenolphthalein end point?

S9. Eight different samples ($A \dots H$) contain only NaOH and/or Na_2CO_3 and/or NaHCO_3 and/or inert material. Calculate the sample compositions, if 1.000-g portions of each sample require the following volumes of 0.2000 N HCl for titration to the phenolphthalein and methyl orange end points, respectively. A : 0, 26.23 ml. B : 45.15, 45.15 ml. C : 29.36, 58.51 ml. D : 31.27, 63.27 ml. E : 45.02, 60.05 ml. F : 11.72, 49.61 ml. G : 0.33, 19.91 ml. H : 39.85, 39.95 ml.

Ans. (D) 66.4% Na_2CO_3 , 1.23% NaHCO_3 .

S10. W g of a sample containing NaOH and/or Na_2CO_3 and/or NaHCO_3 and/or inert material requires for titration A_p milliequivalents of HCl to the phenolphthalein end point and A_m milliequivalents of HCl to the methyl orange end point. Express the percentage composition of the mixture in two cases: (a) $A_m > 2A_p$; (b) $A_m < 2A_p$.

S11. Each of the following solutions is prepared by dissolving the substances shown in the table below. Express the composition of each solution as simply as possible.

Ans. (D) 0.500 M Na_2HPO_4 , 0.500 M Na_3PO_4 .

SOLUTION	FORMULA WEIGHTS PER LITER OF SOLUTION					
	HCl	H_2PO_4	NaH_2PO_4	Na_2HPO_4	Na_3PO_4	NaOH
A.....	0.100	0	0.100	0	0	0
B.....	0.100	0	0	0	0.100	0
C.....	0	0.100	0	0.100	0	0.100
D.....	0	0.100	0.200	0.300	0.400	0.500
E.....	0.500	0	0.100	0.200	0.300	0.400
F.....	0.400	0.500	0	0.100	0.200	0.300
G.....	0.300	0.400	0.500	0	0.100	0.200
H.....	0.200	0.300	0.400	0.500	0	0.100
I.....	0.100	0.200	0.300	0.400	0.500	0
J.....	0	x	0	0	y	0

S12. The following table gives titration data for 100-ml aliquots of several solutions, each of which is prepared by dissolving any or all of the following substances in water: HCl, H_3PO_4 , NaH_2PO_4 , Na_2HPO_4 , Na_3PO_4 , NaOH. Calculate the composition of each solution. All blanks are zero.

Ans. (E) 0.01096 M Na_2HPO_4 , 0.02312 M NaH_2PO_4 , NaCl indeterminate.

SOLUTION	REACTION TO		MILLILITERS OF 0.1000 <i>N</i> STANDARD SOLUTION TO REACH			
	M.O.	Phth.	M.O. End Point		Phth. End Point	
			HCl	NaOH	HCl	NaOH
A.....	acid	acid	22.65	28.63
B.....	acid	acid	10.23	30.69
C.....	acid	acid	15.29	30.58
D.....	basic	acid	48.27	38.76
E.....	basic	acid	10.96	23.12
F.....	basic	basic	32.00	16.00
G.....	basic	basic	23.95	0
H.....	basic	basic	28.62	28.62
I.....	basic	basic	49.53	20.78
J.....	acid	acid	38.95	38.95
K.....	acid	acid	<i>z</i>	<i>y</i>

Miscellaneous acid-base titration problems

S1. A solid sample is known to contain only BaO , Ba(OH)_2 , and BaCl_2 . Explain how you would determine the amount of BaO present and how you would calculate the results.

S2. Devise a direct or indirect method for the determination of each of the following substances by titration with standard acid or base: ZnSO_4 ; $\text{Al}_2(\text{SO}_4)_3$; CaO . Discuss the accuracy of each method.

S3. A solution contains only NaBO_2 and/or Na_2CO_3 . Devise a method for analysis that involves titration with standard acid and/or base.

S4. A 0.4325-g sample of benzoic acid requires 45.83 ml NaOH for titration. What is the normality of the NaOH ?

S5. The S in a 1.500-g sample of steel is burned in oxygen to SO_3 , which is absorbed in a trap containing 100.0 ml of 0.0100 *N* NaOH . On back-titrating the excess base, 35.23 ml of 0.0100 *N* HCl are required. What is the % S in the steel?

Ans. 0.69%.

S6. What volume of conc. H_2SO_4 is required to prepare 2.0 l of 0.10 *M* H_2SO_4 ?

S7. An excess of pure conc. HCl is added to a 25.00-ml aliquot of an NaOH solution in a beaker (empty weight, 25.7342 g). The contents are then evaporated and dried. The weight of the beaker and residual NaCl is 25.9876 g. Calculate the concentration of the NaOH solution.

Ans. 0.1734 *N*.

S8. To determine CO_2 in air, a 100-ml aliquot of 0.100 *M* NaOH was placed in a bubbler, and 23.50 l of air at STP were aspirated through the solution. Afterward, the bubbler contents required 47.89 ml of 0.100 *M* HCl for titration from the phenolphthalein to the methyl orange end point. A blank on another 100-ml aliquot of the base solution required 0.47 ml of the standard HCl . Calculate the percentage of CO_2 in the air.

S9. In the determination of C in steel, a 1.50-g sample is ignited, and the CO_2 formed is absorbed in 100.0 ml of 0.01000 *M* Ba(OH)_2 . The excess Ba(OH)_2 is then titrated to the phenolphthalein end point with 0.1000 *N* HCl , 6.27 ml being required. Calculate the % C in the steel. The end point in this method is much sharper than it is when NaOH is used instead of Ba(OH)_2 . Explain (L2).

Ans. 0.549%.

S10. What is the normality of a base solution, if 42.56 ml are required to titrate 2.00 g of primary standard succinic acid, $(\text{CH}_2)_2(\text{COOH})_2$?

S11. What is the percentage of citric acid in a 1.000-g sample that requires 23.02 ml of standard base for titration? 1.000 ml of the base is equivalent to 19.32 mg of sulfamic acid.

Ans. 29.33%.

S12. Glacial acetic acid consists only of acetic acid (CH_3COOH) and a small amount of acetic anhydride ($(\text{CH}_3\text{CO})_2\text{O}$). When dissolved in water, the anhydride forms acetic acid. A sample of the mixture weighing A grams is dissolved in water and requires B ml of C N NaOH for titration. Set up an expression for the percentage of acetic anhydride in the sample in terms of A , B , and C .

S13. An unlabeled bottle of a pure, primary standard, organic acid contains benzoic, sulfamic, KHP, or $\text{H}_2\text{C}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. A 1.00-g sample requires 48.90 ml of 0.1000 N NaOH for titration. Which acid does the bottle contain? Give a simple, quick way to confirm the conclusion qualitatively. *Ans.* KHP.

S14. What is the equivalent weight of an organic acid, 1.000 g of which requires 27.23 ml of 0.1000 N NaOH ?

S15. Give the citric acid titer of 0.1000 N NaOH . *Ans.* 6.40 mg/ml.

S16. An Na_2CO_3 - NaCl mixture contains 26.25% Na_2CO_3 . Express this as an equivalent percentage of Na_2O .

S17. Azeotropic HCl , prepared by distillation at 750 mm pressure, contains 20.245% HCl by weight. How much of the azeotropic mixture is required to prepare 2.000 l of 0.1000 N HCl ? *Ans.* 36.02 g.

S18. What is the concentration of the solution prepared by diluting 22.96 g of the azeotropic solution of Prob. S17 to 1.000 l?

S19. Assuming that volumes are additive, what is the normality of a solution prepared by mixing 10.56 ml of 0.102 M NaOH with 23.25 ml of 0.156 M Na_2CO_3 ? Do the answers need any qualifications? *Ans.* 0.139 N (to phenolphthalein); 0.246 N (to methyl orange).

S20. Describe how 0.5023 N H_2SO_4 should be diluted to give 0.5000 N H_2SO_4 . Approximately a liter is desired.

S21. In what proportions should 1.072 M HCl and 1.535 M HCl be mixed to give 1.500 M HCl ? What assumption is made in preparing such a mixture? What further work is necessary if it is desired not to make this assumption?

Ans. 0.924 ml of 1.535 M to 0.076 ml of 1.072 M .

S22. A mixture containing only Na_2CO_3 and K_2CO_3 weighs 1.0000 g. Calculate the percentage of each carbonate in the sample if 35.52 ml of 0.5000 N HCl are required for direct titration to the methyl orange end point.

S23. A 1.00-g sample of an MgSO_4 - K_2SO_4 mixture is weighed into a 100-ml volumetric flask. About 40 ml of distilled water are added to dissolve the sample. Then 50.00 ml of 0.2000 N NaOH are added to precipitate $\text{Mg}(\text{OH})_2$, and the resulting mixture is diluted to 100.0 ml, mixed well, and allowed to settle. Withdrawal and titration of a 50.00-ml aliquot of the clear supernate requires 10.23 ml of 0.2000 N HCl . All materials are carbonate-free, and blanks are zero. Calculate the percentage of MgSO_4 in the sample. *Ans.* 35.6%.

S24. KNO_3 in a KCl - KNO_3 sample is reduced to NH_3 in alkaline solution, and the NH_3 is distilled into boric acid solution (Winkler method). The NH_3 in the distillate is titrated directly with standard HCl . What should be the HCl normality, in order that each milliliter should be equivalent to ten milligrams of KNO_3 in the sample?

REDOX STOICHIOMETRY AND EQUILIBRIA

E° FOR A RESULTANT HALF-REACTION

(See Sec. 19B, p. 398)

By combining half-reactions, the TSP may be extended, since the E° values of the resultant half-reactions may be calculated simply from the E° values of the component half-reactions, using the following rules. Proof of these rules is beyond the scope of this book, but may be found in any text of physical chemistry (D1). (1) Multiplying a half-reaction throughout by any factor does not change E° . (2) Reversing the direction of a half-reaction changes the sign of E° . Thus E° for $\text{I}_2 + 2e \rightleftharpoons 2\text{I}^-$ is 0.5355 v, whereas E° for $2\text{I}^- \rightleftharpoons \text{I}_2 + 2e$ is -0.5355 v. (3) For a resultant half-reaction obtained by adding several component half-reactions, E° is

$$n_r E_r^\circ = n_1 E_1^\circ + n_2 E_2^\circ + \cdots$$

E_r° and n_r are the E° value and the number of electrons for the resultant half-reaction, while E_1° , n_1 , etc., represent these values for each of the component half-reactions.

Example S1. To calculate E° for the $\text{VO}_2^+ \text{-V}^{2+}$ half-reaction formulated in Ex. 1, page 399,

$$E^\circ_{\text{VO}_2^+ \text{-V}^{2+}} = \frac{1}{3}(-0.255 + 0.361 + 1.00) = 0.369 \text{ v}$$

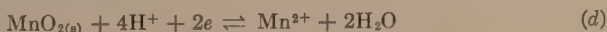
Example S2. Calculate E° for the $\text{MnO}_2 \text{-Mn}^{2+}$ half-reaction, given the E° values for the $\text{MnO}_4^- \text{-Mn}^{2+}$ and $\text{MnO}_4^- \text{-MnO}_2$ half-reactions.



Reversing the direction of Eq. *a*,



Adding Eqs. *b* and *c* and simplifying,



Calculating E° for reaction d from the E° 's of reactions b and c ,

$$E^\circ_{\text{MnO}_2\text{-Mn}^{2+}} = \frac{1}{2}[5(1.51) - 3(1.695)] = 1.23 \text{ v} \quad (e)$$

This checks the value given in the TSP.

USE OF ACTIVITIES IN THE NERNST EQUATION

(See Sec. 19D.2b, p. 406)

Instead of molar concentrations in the mass-action expression $Q_{\text{ox}}/Q_{\text{red}}$ of Eq. 19.7 (p. 406), activities should be used. As an example, $Q_{\text{ox}}/Q_{\text{red}}$ for the reaction of 19.6 is

$$\frac{Q_{\text{ox}}}{Q_{\text{red}}} = \frac{(a_{\text{A}_{\text{ox}}})(a_{\text{B}})^b \dots}{(a_{\text{A}_{\text{red}}})(a_{\text{D}})^d \dots} \quad (Sa)$$

In terms of molar concentration and the activity coefficient (p. 701), the activity of any species, i , is

$$a_i = [i]\gamma_i \quad (Sb)$$

Activity coefficients for ionic solutes may be found in Appendix VI (p. 921). Activity coefficients for undissociated molecules, including dissolved gases, may be approximated as unity at low ionic strengths and at pressures less than a few atmospheres.

Two of the illustrative examples of Chapter 19 are reworked below, with corrections for activity effects.

Example S1. Although the answers to Ex. 1, page 411, are only approximate, they may be used to estimate activity coefficients of the reacting species in the equilibrium system. These estimated activity coefficients are then used to obtain a second set of answers that is more accurate than the first. This process is repeated until a consistent set of answers is obtained. Not many approximations are necessary, for, as this example shows, the ionic strength and activity coefficients do not often change greatly as a result of chemical reaction.

$$\left(\begin{array}{c} \text{Ionic strength} \\ \text{at equilibrium} \end{array} \right) = \frac{1}{2}(0.007 \times 2^2 + 0.0063 \times 1^2 + 0.0105 \times 2^2) = 0.038 \text{ M}$$

From Appendix VI,

$$\gamma_{\text{Cd}} = 0.51 \quad \gamma_{\text{Tl}} = 0.82$$

Defining y in the same way as before, but using activity coefficients in the equilibrium-constant expression, gives

$$\frac{[0.82(0.0010 + 2y)]^2}{0.51(0.010 - y)} = 0.0054$$

Solving this equation by trial and error gives $y = 0.0023 \text{ M}$, instead of 0.0026 M as in Ex. 1.

The equilibrium composition is therefore

$$[\text{Cd}^{2+}] = 0.010 - 0.0023 = 0.008 \text{ } M$$

$$[\text{Tl}^+] = 0.0010 + 2(0.0023) = 0.0056 \text{ } M$$

$$[\text{SO}_4^{2-}] = 0.0105 \text{ } M$$

Cd metal precipitated per liter of solution is 0.0023 mole. Tl metal also exists in the system, since it was added in excess.

A recalculation of ionic strength from this better composition gives a more accurate value of 0.040 M , instead of 0.038 M as before. Second approximations of the activity coefficients differ so little from the first values that no further calculations are necessary.

Example S2. Work Ex. 1, page 421, correcting for activity effects.

The M^{2+} concentration of $2.3 \times 10^{-14} \text{ } M$, calculated from the E , is really an activity and not a molar concentration.

The chloride activity may be calculated in 0.025 M KCl,

$$a_{\text{Cl}} = [\text{Cl}^-]\gamma_{\text{Cl}} = 0.025(0.85) = 0.0212 \text{ } M$$

\uparrow
 γ_{Cl} in a solution with ionic strength 0.025.

The activity product for MCl_2 is therefore

$$K_s^\circ = a_{\text{M}}(a_{\text{Cl}})^2 = 2.3 \times 10^{-14}(0.0212)^2 = 1.03 \times 10^{-17}$$

The assumptions made in working this problem should be noted. First, the activity of M^{2+} is calculated on the assumption that there are no polarization or junction potentials included in the E of -0.350 v . Second, the average activity coefficients from Appendix VI give only an approximation of a_{Cl} . A better value of a_{Cl} could be found experimentally, or from the literature.

Assumptions would also be involved in the use of the calculated K_s° . With only the given data, it would be necessary to assume that solutions of MCl_2 are describable by only the one equilibrium for which the solubility product is known, and that there are no appreciable amounts of other soluble species containing M^{2+} and/or Cl^- (such as MCl^+ , MCl_2 , or MCl_3^-). This would be a risky assumption, and, in general, a value for a usable activity product would not be based on a measurement at a single composition, as in this problem. The proper procedure would be to measure the activity product over a range of compositions, to indicate whether or not more than one equilibrium would be necessary to describe the solution.

REDOX KINETICS

(See Sec. 19F, p. 424)

The Mechanism of Redox Reactions (D11)

It is very important to distinguish between the stoichiometry and the mechanism of a reaction. The balanced equation for the oxidation of Fe^{2+} by $\text{Cr}_2\text{O}_7^{2-}$ gives the weight relationships, or *stoichiometry*, between the various reagents and products.



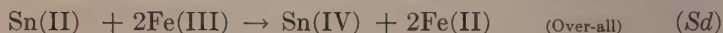
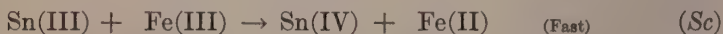
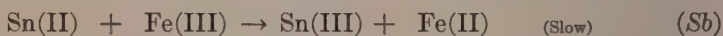
However, the over-all equation tells nothing about the *mechanism* of the reaction—that is, the order in which the various reagents combine, and their rates of combination.

Invariably, an over-all reaction that involves a combination of more than two or three molecules never takes place in one step. In reaction *Sa* above, the one-step combination would involve the simultaneous collision and reaction of six Fe^{2+} 's, one $\text{Cr}_2\text{O}_7^{2-}$, and fourteen H^+ 's, which is an exceedingly improbable event.

Rather, the over-all reaction is conceived to occur via a stepwise series of *bimolecular* reactions, that is, reactions involving two reacting molecules. Termolecular reactions, involving three molecules, are not often postulated in mechanisms, because they are improbable. Instead of a termolecular process, two or more consecutive bimolecular processes will usually take place. However, termolecular reactions involving a solvent molecule are sometimes postulated because the solvent molecules are always in high concentration and therefore do not limit the rate of the process.

There is good evidence that those electron-exchange reactions are most rapid in which the electron acceptor atom can exactly accept all of the electrons given by the donor atom.

Thus, the oxidation of Sn(II) by Fe(III) does not occur in a single termolecular step, but has been shown to occur as follows:



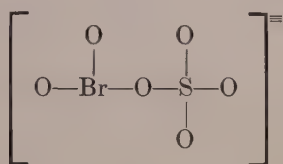
Each of the steps has its own characteristic rate, and the rate of the over-all reaction is limited by the slowest step.

The stepwise mechanism proceeds through the formation of *intermediates* that are highly reactive and transitory ions or free radicals, and that exist only while the reaction is in progress. Sn(III) is the reactive intermediate in the mechanism *Sb–Sd* above. Because of their instability, the reactive intermediates can seldom be observed by ordinary analytical techniques; instead, their existence and properties are usually inferred from reaction rate and mechanism studies. Some typical reactive intermediates that have been postulated in aqueous solution mechanisms are HO , HO_2 , Cl_2^- , Br_2^- , I_2^- , IOH^- , Fe(IV) , Sn(III) , Mn(V) , Cr(IV) , Cr(V) , Tl(II) , CO_2^- , and C_2O_4^- .

In general, when a chemical reaction occurs, the reactant molecules

come together to form an *activated complex* that is stable enough and that lasts long enough for the reaction (i.e., changes in chemical bonding) to occur. During the bonding changes, the reactants lose their identities to become the products, and the activated complex breaks up to give the individual products.

In a redox reaction, there is an electron transfer from the reductant to the oxidant in the activated complex. A fundamental question concerns the mode of transfer of the electron. If the oxidant and reductant ions are of unlike charge, a close approach of the two is favored, permitting an easy transfer of the electron, and the reaction is rapid. If the oxidant and reductant ions are of like charge, however, their repulsion does not permit an approach close enough for electron transfer. In such cases, the electron is conceived to transfer via a bridge of intermediate atoms that are also a part of the activated complex. Sometimes, the bridging atoms are furnished by the reacting moieties themselves. Thus, the activated complex in the oxidation of SO_3^- by BrO_3^- has been postulated to be



Often, however, another species may provide the bridge. Thus, the above oxidation of Sn(II) by Fe(III) does not occur at a measurable rate in dilute perchlorate solution, even at 70°C . The lack of reaction is apparently due to the repulsive forces between the highly charged hydrated positive ions. In chloride medium, however, the reaction occurs in a few minutes. Chloride has a negative charge and a good tendency to complex with both Fe(III) and Sn(II) . In the activated complex, Sn(II) and Fe(III) are conceived to be linked together with chloride, through which the electron transfer can occur.

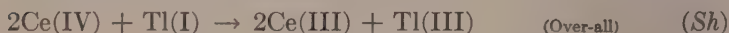
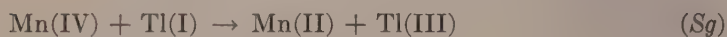
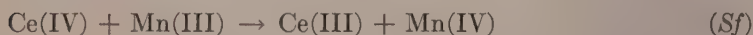
Not all solute species have equal efficiencies as electron transfer bridges. Effective bridging atoms are ones that have at least two unshared pairs of electrons and that tend to complex with both the oxidizing and reducing atoms. Systems with conjugated double bonds are good bridges for electron transfer.

The bridging hypothesis explains observations on many different kinds of redox reactions, including reactions between two cations, and also between two anions. On the other hand, there are some reactions, like the rapid electron exchange between Fe(CN)_6^{4-} and Fe(CN)_6^{\equiv} , that are not satisfactorily explained by the bridge hypothesis.

Catalysis (D10)

The catalytic process is described in general terms on page 31. More specifically, the role of a catalyst is to give an activated complex that reacts more easily and rapidly than the activated complex formed without the catalyst. The catalyst is regenerated as fast as it is used in the reaction, and there is no net disappearance or formation of the catalyst. In the above oxidation of Sn(II) by Fe(III), chloride is a catalyst.

Sometimes the catalyst acts as a reactive intermediate, permitting the reaction to follow an easier and faster path than can be followed in the absence of the catalyst. Thus, Ce(IV) oxidizes Tl(I) very slowly, the time required for half-reaction being over 1000 hours at room temperature. MnSO₄ catalyzes the reaction, probably according to the following mechanism, so that the time for half-reaction is only about an hour at room temperature.



The Mn(II) catalyzed oxidation of As(III) by Ce(IV) is believed to proceed by the same mechanism. The catalytic action of Ag(II) in persulfate oxidations is discussed on page 818.

Induced Reactions (L2, M12)

An elementary description of induced reactions is given on page 32, which should be studied for terminology and definitions.

The extent of induction is described by the induction factor, F_i :

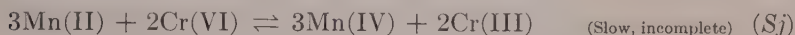
$$F_i = \frac{\text{equivalents of induced reaction}}{\text{equivalents of primary reaction}} \quad (Si)$$

Two classes of induced reactions are recognized, based on the magnitude of the induction factor. In a *coupled reaction*, F_i approaches a small integer or simple ratio, like 1, 2, or $\frac{1}{2}$, as the ratio of acceptor to inductor becomes large. In an *induced chain reaction*, F_i is large, and may increase without limit as the ratio of acceptor to inductor becomes large.

Induced reactions are potentially sources of great error in titrations, as shown in the following sections.

Coupled reactions. The oxidation of a substance by dichromate may be induced in a variety of ways. Thus, the slow oxidation of I^- by $\text{Cr}_2\text{O}_7^{=}$ may be induced by the reaction between $\text{Cr}_2\text{O}_7^{=}$ and a variety of inductors, such as Fe(II) , As(III) , V(IV) , V(III) , V(II) , Ti(III) , and U(IV) . Also, an inductor may be capable of inducing several reactions. Thus, the reaction between As(III) and Cr(VI) can induce the slow oxidations of I^- , Mn(II) , and tartaric acid by Cr(VI) .

A very interesting example of a coupled reaction is the oxidation of Mn(II) by Cr(VI) , induced by the Cr(VI) - As(III) reaction. The direct oxidation of Mn(II) by Cr(VI) does not occur significantly at room temperature. Not only is the rate negligible, but inspection of the TSP shows that the reaction is not even quantitative.



In a system containing Mn(II) , As(III) , and Cr(VI) , however, oxidation of Mn(II) to Mn(IV) is induced by the following mechanism.



The Cr(IV) formed in the primary reaction Sk may react according to either of two paths: It may follow reactions Sl and Sm to give a total of $1\frac{1}{2}$ As(V) 's per Cr(VI) used. Or, the Cr(IV) may follow reactions Sn and So to give a total of 1 As(V) and $\frac{1}{2}$ Mn(IV) per Cr(VI) used. For the path Sk , Sl , and Sm , F_i is zero, while for the path Sk , Sn , and So , F_i is $\frac{1}{2}$.

Which of the two paths is followed depends on the rates of the various steps. Actually, the rate of step Sn is much greater than the rate of the competing step Sl , and experimental induction factors approaching $\frac{1}{2}$ are easy to achieve.

The implications in the preceding discussion are worth restating clearly and definitely. Through the coupled mechanism, a reaction (Eq. Sj , the oxidation of Mn(II) by Cr(VI)) is brought about, that by itself is not only slow, but actually unfavorable energetically.

Study of the preceding mechanism also reveals the induced reaction as an insidious source of error in analytical determinations. Suppose that a sample contains Mn and As , and that a worker wants to determine the As content by reduction to As(III) and titration with standard

Cr(VI). If he knows nothing about induced reactions, he might check the behavior of Mn, to find that it does not react with dichromate, and to conclude that the Mn need not be removed from the sample before titrating the As. In the mixture, however, the induced oxidation of Mn(II) can occur, using up standard dichromate, and causing the calculated As content to be high. Titration errors of several hundred per cent can be caused by induced reactions.

The error caused by an induced reaction in a titration is not so simple as that caused by a side reaction, which is often constant, and which can often be corrected for by a blank. The induced reaction error is variable; it not only depends critically upon all factors that affect reaction rates, but it also depends on the concentrations of the inductor and acceptor, and cannot be corrected for by a simple blank determination.

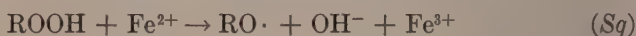
The only way to diminish error due to an induced reaction is to remove the acceptor before titration, or to suppress the induced reaction (*vide infra*).

Induced chain reactions. Very large induction factors may be observed if the mechanism involves a chain reaction. An interesting and thoroughly studied reaction is the reduction of peroxides by Fe(II), analytically important because it is the basis of a method for determining H_2O_2 and organic peroxides (ROOH).

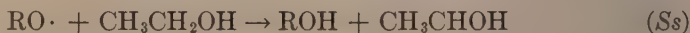
The stoichiometric or over-all reaction is



The mechanism by which the over-all reaction occurs is



Samples containing organic peroxides also contain other oxidizable organic substances. In the presence of such an oxidizable substance, say ethyl alcohol ($\text{CH}_3\text{CH}_2\text{OH}$), and in the absence of air, the $\text{RO}\cdot$ free radicals initiate a chain (Eqs. *Ss*, *St*, *Sq*), which can propagate to consume ROOH and $\text{CH}_3\text{CH}_2\text{OH}$ indefinitely, until the chain is terminated by Eq. *Sr*.

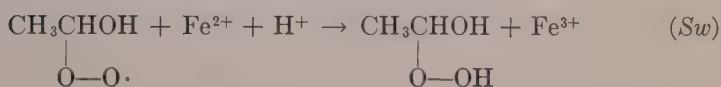
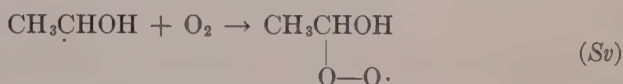


The over-all oxidation of ethyl alcohol by ROOH, induced by the peroxide- Fe^{2+} reaction, is the sum of Eqs. *Ss*, *St*, and *Sq*:

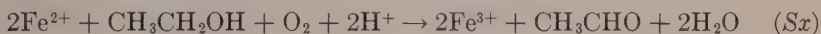


Reaction *Ss*, which initiates the chain, is considerably faster than the chain-terminating reaction *Sr*, which makes for a long chain. If the chain is long, many more moles of ROOH are reduced by $\text{CH}_3\text{CH}_2\text{OH}$ than are reduced by the desired stoichiometric reaction with Fe^{2+} . Therefore, any calculation of the ROOH content that is based on the Fe^{2+} used in titration gives low results.

In the presence of air, the organic free radical formed in Eq. *Ss* may suffer oxidation to a peroxide, initiating another chain (Eqs. *Sv* and *Sw*, followed by reactions of the peroxide similar to Eqs. *Sq* and *Ss*):



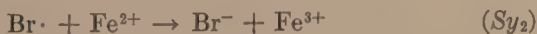
Summation of this chain leads to the following over-all reaction, in which Fe^{2+} and also $\text{CH}_3\text{CH}_2\text{OH}$ are air-oxidized.



In short, Fe^{2+} is used in a reaction other than with the sought-for ROOH, leading to high results.

Of course, the presence of air does not exclude the previously described chain *Ss*, *St*, and *Sq*, leading to the over-all reaction *Su*, and to low results. Which of the two chains predominates, and whether the results are low or high, depends upon the proportions of the free radical $\text{CH}_3\dot{\text{C}}\text{HOH}$ entering the competing reactions *St* and *Sv*. If the O_2 concentration is high compared to the Fe^{3+} concentration, reaction *Sv* is favored, leading to the over-all equation *Sx* and high results. If the Fe^{3+} concentration is high compared to the O_2 concentration, reaction *St* is favored, leading to the over-all equation *Su* and low results. Depending on conditions, peroxide contents ranging from only 17% of the true value (in the absence of air) to 690% of the true value have been measured.

There are two ways of eliminating the error due to the induced reactions. Through the addition of Br^- , the error-causing chains can be broken. Br^- reacts much more avidly with the free radical $\text{RO}\cdot$ than does ethyl alcohol, and reaction *Ss* does not occur significantly.



The sum of Eqs. Sy is Sr and so the over-all effect of Br^- is not only to suppress the error-causing chains, but also to bring about the desired stoichiometrical reaction Sp , where $ROOH$ and Fe^{2+} react in the ratio 1:2.

Br^- and Cl^- are good suppressors in the absence or presence of air. Acetone and acetic acid are also chain suppressors, but are effective only in the absence of air.

In another method, an unsaturated compound, like acrylonitrile ($CH_2=CHCN$), reacts more efficiently with $RO\cdot$ (Eq. Sz_1) than does ethyl alcohol, to stop the error-causing chains. In the following mechanism, Eqs. Sz_2 and Sz_3 represent the chain polymerization of the monomer, and Eq. Sz_4 represents the chain termination.



In the presence of acrylonitrile, the $RO\cdot$ from Eq. Sq reacts exclusively with the acrylonitrile, and none according to the competing reactions Sr and Ss . In the presence of acrylonitrile, the over-all reaction is the sum of Eqs. Sq and Sz , or



The $ROOH$ and Fe^{2+} react in the ratio 1:1, stoichiometrically.

In summary, the suppressors work to eliminate the nonstoichiometrical chains that cause error, and to substitute stoichiometrical reactions in their stead.

SUPPLEMENTARY QUESTIONS

Section 19F

S1. A necessary requirement of a redox catalyst is that its E should lie between the E 's of the two half-reactions constituting the over-all reaction to be catalyzed (**K16**). Give a specific example illustrating this statement. What might be the mechanism of catalysis in this example?

S2. Is the requirement of Ques. S1 sufficient for catalysis? Explain.

S3. Give a speculative explanation of the low formal potential of the $Cr(VI)$ - $Cr(III)$ system in H_2SO_4 (Appendix IX).

S4. Sum the steps Sv , Sw , Sq , and Ss to obtain the over-all reaction Sx .

S5. In the peroxide-Fe(II) reaction, explain carefully the difference in behavior of the ethanol under anaerobic and aerobic conditions.

SUPPLEMENTARY PROBLEMS

Section 19D

S1. Rework one part of Prob. 2, Sec. 19D (p. 433), correcting for activity effects. *Ans.* (c) 0.270 v.

S2. Rework one of Probs. 11, 12, 13, 17, or 18 in Sec. 19D (p. 434), or 15-18 in Sec. 19E (pp. 436-37), correcting for activity effects.

Section 19E

S1. Calculate the practical work performed by the cell of Ex. 3, page 421, if it is permitted to discharge to equilibrium. An outline of the calculation follows: (a) Express $[Ag^+]$ and $[Zn^{2+}]$ as functions of the coulombs of electricity, y , passed. (b) Express the E of each electrode as a function of the coulombs of electricity passed, using the results of step a. (c) The cell voltage, V , at the instant when y coulombs of electricity have been passed is the difference of the two E 's of step b. (d) The practical work performed in operating the cell until equilibrium is reached may be found by integrating

$$\int_0^{\text{equil}} V dy = \int_0^{13,000} \left[E_{Ag^+}^\circ - E_{Zn^{2+}}^\circ + 0.0591 \log \left(0.090 - \frac{y}{1.5 \times 96,496} \right) - \frac{0.0591}{2} \log \left(0.050 + \frac{y}{4 \times 96,496} \right) \right] dy$$

S2. Suppose that the internal and external resistances of the cell of Prob. S1 are 2,000 and 10,000 ohms, respectively. What fraction of the work is utilized usefully in the external circuit?

Section 19F

S1. In the determination of As(III) by titration with standard Cr(VI), what is the maximum error that could be caused by the induced oxidation of Mn(II)?

Ans. As content could be too high by as much as 50%.

S2. In the determination of Sn(II) by titration with standard Cr(VI), an induced air oxidation of the Sn(II) is observed. If the induction factor is 57, calculate the relationship between the true and observed Sn contents.

S3. The otherwise slow oxidation of I^- by $Cr_2O_7^{2-}$ is induced by the reaction between Fe^{2+} and $Cr_2O_7^{2-}$, according to the following mechanism. Find the limiting value of the induction factor as the ratio of I^- to Fe^{2+} becomes large.



Ans. 2.

REDOX TITRATIONS

PREOXIDATION AND PREREDUCTION

(See Sec. 20A.3, p. 440)

Preoxidants

Sodium peroxide (Na_2O_2) is used in fusions as an oxidizing flux. Chromium in ores is oxidized to chromate (p. 474). Fusion with Na_2O_2 in the Parr bomb is employed in the analysis of organic compounds for S, halogens, etc. (p. 735). To decompose the excess Na_2O_2 , the melt is dissolved in water and the solution is boiled for a few minutes.



Hydrogen peroxide (H_2O_2) is available commercially as Superoxol (30% H_2O_2). It is a good oxidant in alkaline solution, in which Cr is oxidized to chromate. The excess H_2O_2 may be destroyed by boiling.



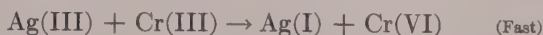
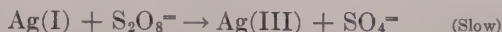
In acid solution, H_2O_2 is a reducing agent, and reduces Cr(VI) to Cr(III), Mn(VII) to Mn(II), etc. Hence, when used as an oxidant in basic solution, all excess of H_2O_2 must be carefully destroyed by boiling the basic solution. If this is not done, reduction of the sought-for substance by the remaining excess of H_2O_2 may occur on acidification.

Potassium persulfate, or peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) is a powerful oxidant in acid solution. Cr(III) is oxidized to Cr(VI), Ce(III) is oxidized to Ce(IV), and Mn(II) is partially oxidized to Mn(VII). Excess persulfate is easily decomposed by being boiled for a few minutes.



The mechanism of persulfate oxidations has been thoroughly studied (D3). Cr(III), V(IV), N_2H_5^+ , Ce(III), and Mn(II) are not oxidized at appreciable rates by persulfate alone. In the presence of a silver salt, however, they all are oxidized at about the same rate by persulfate. To account for the rate being independent of the reductant concentration, the slow step in the mechanism is postulated to be the oxidation

of Ag(I) to Ag(III) by persulfate. The strongly oxidizing Ag(III) then reacts rapidly with the reductant:



Sodium bismuthate (NaBiO_3) is strong enough to oxidize Mn(II) to Mn(VII) in acid solution. The oxidizing substance seems to be Bi_2O_5 or Bi_2O_4 . The excess bismuthate is insoluble and easily removed by filtration (A12).

Ozone (O_3) cannot be stored and requires special equipment for generation, but it is a useful and powerful preoxidant (W5). After pre-oxidation, excess ozone and oxygen may be easily removed by boiling the solution, or by passing an inert gas such as CO_2 through it. AgNO_3 is often required as a catalyst to speed the oxidation. Mn is quantitatively oxidized to Mn(VII), Ce to Ce(IV), V to V(V), and Cr to Cr(VI) in acid solution. Se and Te are quantitatively oxidized to selenate and tellurate in alkaline solution, but only partially in acid solution. Sb and As are quantitatively oxidized to the pentavalent states in either acid or alkaline solution. Co(OH)_2 and Ni(OH)_2 are oxidized to Co(OH)_3 and Ni(OH)_3 .

Perchloric acid (HClO_4) is commercially available in concentrations of 60% and 72%, the latter being an azeotropic mixture.

Hot 72% HClO_4 is a very powerful oxidant (S17), capable of oxidizing Cr to Cr(VI) and V to V(V). Sulfur in S-bearing samples is oxidized to sulfate without loss by volatilization, which often occurs when other preoxidants are used. Similarly, in As- and Sb-bearing samples, the As and Sb are rapidly oxidized to the pentavalent state, without loss as volatile trivalent compounds.

On the other hand, the oxidizing power drops rapidly as the temperature or concentration decreases. Thus, at 25°C, even 72% HClO_4 does not oxidize iodide. Even at the boiling point, 50% HClO_4 does not oxidize Fe(II), except very slowly.

HClO_4 is very useful as a preoxidant. To carry out a preoxidation, the solution is evaporated with HClO_4 until fumes of HClO_4 begin to come off, indicating that the powerful oxidizing composition of 70% HClO_4 has been attained. After the solution is boiled for a short time, oxidation is complete. The mixture is then cooled and diluted, whereupon the oxidizing power of the HClO_4 becomes negligible. The oxidized sought-for constituent may then be determined by titration with a standard reducing solution, with which the dilute HClO_4 does not react. Chromium in an ore may be preoxidized in this way to Cr(VI). On dilution, the Cr(VI) may be determined with standard FeSO_4 . (In practice, the conc. HClO_4 goes partially to chlorine in the preoxidation step.

The diluted solution must be boiled to drive off this chlorine before the titration with FeSO_4 .)

HClO_4 is particularly useful in the oxidation of organic samples. As a first step, the organic matter must ordinarily be destroyed before determination of most elements. Such procedures are called *ashing procedures*. In *dry ashing*, the organic sample is ignited, usually with a flux to retain the sought-for elements. The fusion with Na_2O_2 in a Parr bomb (p. 735) is a dry-ashing procedure. In *wet ashing*, the sample is decomposed by being heated with a mixture of oxidizing acids. Wet ashing with mixtures containing HClO_4 is often more smooth, rapid, and complete than with other acid mixtures. The HClO_4 must be used in admixture with another acid (H_2SO_4 , H_3PO_4 , or HNO_3) to prevent explosion, and catalysts (Os or V) are sometimes used to increase the rate of decomposition. Detailed instructions for the wet ashing of diverse kinds of samples are given in the literature (D6).

HClO_4 is safe to use with the proper precautions (S23). However, it must be classed as a hazardous reagent because violation of any of these precautions may lead to disaster. Even though it is not possible to attain the explosive composition (85% HClO_4) simply by evaporation of dilute solutions, severe explosions involving HClO_4 have been traced to its contact with organic matter. While certain oxidations may be carried out very efficiently with HClO_4 , such procedures should not be used routinely without proper precautions in both use and disposal. For instance, HClO_4 solutions should never be routinely evaporated into hood systems, where the HClO_4 might accumulate, become mixed with organic dust, and explode. For these reasons it is not used in elementary student experiments.

Prereductants

Reducing metals and amalgams are convenient prereducers because their insolubility prevents accumulation of any excess of reducing agent. There are essentially three ways in which metals may be used as prereducers.

1. The most common method of reduction is to pass the solution through a column containing the metal in granulated form. The Jones reductor is a column containing granulated amalgamated* Zn. Because

*Zinc metal reacts with dilute acids to liberate hydrogen gas. The purpose of amalgamation is to reduce the rate of liberation of hydrogen gas from acid solutions, allowing reduction of the sought-for constituent in acid solution. Mossy Zn may be amalgamated by being shaken for a few minutes with a solution of HgCl_2 . The HgCl_2 is reduced to Hg metal, which coats the Zn particles. The preparation of the Jones reductor is described in many texts (S36).

Zn is such a powerful reducer, its action is not very selective (Table S20.1, p. 822). In addition, the Zn reductor is subject to several limitations.*

To obtain less powerful reducing action, less active metals than Zn may be used, such as Cd, Pb, Bi, and Ag. The Walden reductor is a column filled with metallic Ag (W3). Silver metal alone is a weak reducer; though it is fairly effective in HCl solutions, it is not nearly so strong as Zn.

2. An active metal as a prereducer is sometimes introduced into the solution in the form of a rod or wire spiral. This procedure is simpler than the use of a column or a liquid amalgam, but is less efficient, since contact between the liquid and solid phases is not so intimate. A Zn spiral may be used to prereducer iron (W14).

It is sometimes advantageous to shake the solution with a finely powdered metal, and to filter the metal out after prereduction. Thus Fe may be reduced to Fe(II) in the presence of Ti(IV) with Cu powder (S15).

The use of Devarda's alloy to reduce nitrates in alkaline solution is described in Exp. 18.6 (p. 378).

3. The active metal may be introduced in the form of a liquid amalgam. Good contact between the amalgam and solution is obtained by their being shaken; if shaken in a separatory funnel, the phases may be easily separated after reduction. The reducing power of the amalgam depends largely upon the activity of the metal. Zn, Cd, Pb, and Bi are commonly used (see Table S20.1). The reducing power of a given amalgam may be controlled by varying the acidity and temperature.

*It is instructive to examine these limitations: (1) Reduction cannot be made in solutions containing nitrate, which is reduced to a mixture of lower oxidation states, hydroxylamine (NH_2OH) being one of the products. NH_2OH is itself a good reducer, and may react with the standard oxidizing solution used to titrate the reduced sought-for substance, causing error in the determination. (2) Oxygen from the air is reduced to H_2O_2 , which is a reducer and causes error just as does NH_2OH . Air should never be drawn into the column, and the liquid level should never be allowed to fall below the top of the Zn. (3) HCl solutions slowly liberate hydrogen by reaction with amalgamated Zn, and are not so appropriate as H_2SO_4 solutions. (4) In some analyses the products react very avidly with oxygen in the air, and the titration must be carried out under an inert atmosphere. Determination of Cr and Ti—by titration after reduction to Cr(II) and Ti(III)—must be made in this way. A simple technique for avoiding titration in an inert atmosphere is to deliver the reduced effluent solution directly beneath the surface of a solution of a ferric salt (e.g., FeCl_3). The reduced substance reacts with Fe(III), forming an equivalent amount of Fe(II), which may then be titrated with the standard oxidizing solution. Only ordinary precautions are necessary, since Fe(II) does not react rapidly with air.

A comprehensive study on the properties of liquid amalgams as prereductants has been made by Someya (S23a).

TABLE S20.1
PREOXIDIZERS AND PREREDUCERS*

Preoxidizers	Oxidation States to Which Some Elements Are Taken†											Approximate <i>E</i> in Presence of Moderate Amounts of Products	Method of Destroying or Inactivating Excess
	Fe	Ti	V	Cr	Mn	Mo	Ce	Co	Ni	U	W		
HClO ₄ (70%, hot).....			5	6	<7							2.0 v	Dilute with water. Boil to remove excess chlorine.
K ₂ S ₂ O ₈ (hot, acid solution, AgNO ₃ catalyst).....	3	4	5	6	7‡		4	3	3			2.0	Boil.
H ₂ O ₂ (in basic solution)....				6								1.8	Boil.
Ozone (acid solution, AgNO ₃ catalyst)			5	6‡	7		4					2.0	Boil, or pass inert gas through solution.
KIO ₄ (acid solution, hot)...				6‡	7		4‡	3‡				1.7	Precipitate Hg ₂ (IO ₃) ₂ , also Hg(IO ₃) ₂ .
NaBiO ₃ (acid solution, hot)					7							1.6	Filter off excess.
PbO ₂ (acid solution, hot)...					7							1.7	Filter off excess.
KClO ₃ (acid solution).....	3				3,4							1.5	Boil in acid solution.
KMnO ₄ (acid solution)....													Boil with HCl, or warm with NaNO ₂ .
Prereducers													
Zn.....	2	3	2	2	2	3	3			3,4		-0.8	Filtration or decantation.
Amalgams: Zn.....	2	3	2	2		3				3	3	-0.8	Separate insoluble liquid amalgam.
Cd.....	2	3	2	3		3						-0.4	
Pb.....	2	3	4	3		3,5				3,4	3	-0.1	
Bi.....	2	4	4	3		3,5				4	5	0.3	Oxidation with HgCl ₂ . Boil, or pass CO ₂ through solution.
SnCl ₂ (in HCl).....	2	3‡	2,3,4			3,5						0.1	
SO ₂	2	4	4	3		3‡						0.1	
Ag (in HCl).....	2	4	4	3	2	5	3			4		0.2	Filtration or decantation.
H ₂ S (in H ₂ SO ₄).....	2	4	4	3		pptd						0.2	Boil, or pass CO ₂ through solution.
Hg (in HCl).....	2	4	4	3		5					5	0.3 v	Separate insoluble Hg.

*Data taken in part from H. Diehl and G. F. Smith, *Quantitative Analysis* (New York: Wiley, 1952), Table 20, with permission of the publisher. More detailed information on these substances is given in other parts of this text and in references S9, S17, S21, and T2.

†The blank spaces in the table signify that behavior of these elements is not mentioned in the references cited.

‡Not complete.

§No statement as to completeness of reaction; may be only partially complete.

||The proportion of the lower valence state produced increases with the acidity. At low acidities, V(IV) or Mo(V) are quantitatively produced; further reduction occurs at higher acidities.

Sulfur dioxide (SO₂) is only a moderately strong reducing agent. While it reduces Fe(III) to Fe(II), it does not reduce Ti(IV), and reduces V only to V(IV). Sb and As are reduced to the trivalent state. The SO₂ may be introduced as a gas stream from tank SO₂, or by the addition of Na₂SO₃ or NaHSO₃ to the acidified solution. The excess may be easily removed by boiling the solution, or by warming and passing a stream of CO₂ through it (V4).

Stannous chloride (SnCl₂) is much used in the determination of Fe in ores. When the Fe is prereduced with SnCl₂ prior to permanganimetric titration, there are fewer interferences than when the Zn reductor is used. SnCl₂ is described more fully in Exp. 20.1 (p. 476).

Selective Reduction

By a choice of prereductants it is sometimes possible to analyze mixtures of sought-for substances without separation. Suppose, for example, that a solution contains Fe and Mo. One aliquot of the solution may be reduced to Fe(II) and Mo(III) by passage through a Zn reductor, while another aliquot may be reduced to Fe(II) and Mo(V) by passage through an Ag reductor. Titration of these two reduced aliquots permits calculation of the Fe and Mo contents of the original solution, as shown in the following example. Other mixtures may be selectively reduced and analyzed in similar manner (see Table S20.1).

Example. A 100.0-ml aliquot (No. 1) of a solution containing Fe and Mo requires 48.26 ml of standard 0.1000 *N* KMnO_4 solution for titration, after passage through a Zn reductor. A second 100.0-ml aliquot (No. 2) requires 42.24 ml of standard KMnO_4 for titration after passage through an Ag reductor. What are the Fe and Mo concentrations in the original solution?

In the titration of aliquot No. 1 with standard KMnO_4 , $\text{Fe(II)} \rightarrow \text{Fe(III)}$, and $\text{Mo(III)} \rightarrow \text{Mo(VI)}$. Hence

$$48.26 \times 0.1000 \left| = \begin{array}{l} \text{(mmoles Fe + 3} \times \text{mmoles)} \\ \text{Mo in 100.0-ml aliquot} \end{array} \right. \quad (a)$$

— meq KMnO_4 used in titration

In the titration of aliquot No. 2 with standard KMnO_4 , $\text{Fe(II)} \rightarrow \text{Fe(III)}$, and $\text{Mo(V)} \rightarrow \text{Mo(VI)}$. Hence

$$42.24 \times 0.1000 \left| = \begin{array}{l} \text{(mmoles Fe + mmoles)} \\ \text{Mo in 100.0-ml aliquot} \end{array} \right. \quad (b)$$

— meq KMnO_4 used in titration

From the difference between Eqs. *a* and *b*,

$$\begin{aligned} (2 \times \text{mmoles Mo in 100.0-ml aliquot}) &= 4.826 - 4.224 \\ \text{mmoles Mo in 100.0-ml aliquot} &= 0.301 \end{aligned} \quad (c)$$

$$\text{Mo concentration} = \frac{0.301}{100.0} = 0.00301 \text{ } M$$

From the difference between Eqs. *b* and *c*,

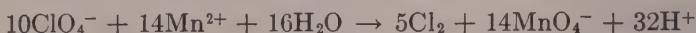
$$\text{mmoles Fe in 100.0-ml aliquot} = 4.224 - 0.301 = 3.923$$

$$\text{Fe concentration} = \frac{3.923}{100.0} = 0.03923 \text{ } M$$

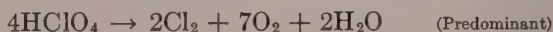
Effect of Rate and Side Reactions on Preoxidation and Prereduction

It should be noted from Table S20.1 that some of the very strongest preoxidants (HClO_4 and $\text{K}_2\text{S}_2\text{O}_8$) are incapable of oxidizing Mn to Mn(VII) quantitatively, while weaker preoxidants (KIO_4) can do so.

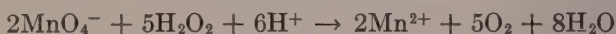
The failure of HClO_4 to oxidize Mn(II) quantitatively to permanganate is due to the complicated behavior of HClO_4 (S19). In the hot, concentrated solution there occurs not only the oxidation reaction



but also other reactions in which the powerful HClO_4 decomposes:



Although the H_2O_2 does not survive long in the strongly oxidizing solution, it is constantly regenerated. Hence at any instant there is always a low, steady-state concentration of H_2O_2 , a reducer which keeps a small proportion of the Mn in the reduced state.



In summary, HClO_4 cannot oxidize Mn(II) quantitatively to permanganate, not because the oxidizing power is too low, but because side reactions prevent complete oxidation.

In acid solution, $\text{K}_2\text{S}_2\text{O}_8$ behaves in a similar manner, H_2O_2 being one of the intermediate decomposition products (T2).

REDOX TITRATIONS

Calculation of E at the Equivalence Point

(See Sec. 20B.1, p. 441)

For certain types of titrations, E at the equivalence point is a simple weighted average of the two E° 's that are involved in the titration, as shown in the following example.

Example S1. Neglecting activity effects, express the equivalence-point potential, in terms of E° values, for the following redox titration of A_{ox} with standard B_{red} .



At the equivalence point

Total eq of A present = total eq of B present

$$\text{eq of A}_{\text{red}} + \text{eq of A}_{\text{ox}} = \text{eq of B}_{\text{red}} + \text{eq of B}_{\text{ox}} \quad (a)$$

Originally, all A is in the form of A_{ox} , and this is used up by reaction with B_{red} according to the above chemical reaction, so that one equivalent of A_{red} is produced for every equivalent of B_{ox} produced. Hence at the equivalence point

$$\text{eq of } A_{\text{red}} = \text{eq of } B_{\text{ox}} \quad (b)$$

$$\text{eq of } A_{\text{ox}} = \text{eq of } B_{\text{red}} \quad (\text{From Eqs. } a \text{ and } b) \quad (c)$$

Since there are α equivalents of A per mole and β equivalents of B per mole, Eqs. *b* and *c* give

$$\alpha(\text{moles } A_{\text{red}}) = \beta(\text{moles } B_{\text{ox}}) \quad \alpha(\text{moles } A_{\text{ox}}) = \beta(\text{moles } B_{\text{red}}) \quad (d)$$

$$\alpha[A_{\text{red}}] = \beta[B_{\text{ox}}] \quad \alpha[A_{\text{ox}}] = \beta[B_{\text{red}}] \quad (e)$$

At the equivalence point,

$$E_{\text{eq pt}} = E_A = E_B$$

$$E_{\text{eq pt}} = E_A^\circ + \frac{0.0591}{\alpha} \log \frac{[A_{\text{ox}}] \cdots}{[A_{\text{red}}] \cdots} = E_B^\circ + \frac{0.0591}{\beta} \log \frac{[B_{\text{ox}}] \cdots}{[B_{\text{red}}] \cdots} \quad (f)$$

$$\alpha E_{\text{eq pt}} + \beta E_{\text{eq pt}} = \alpha E_A^\circ + \beta E_B^\circ + 0.0591 \log \left(\frac{[A_{\text{ox}}][B_{\text{ox}}] \cdots}{[A_{\text{red}}][B_{\text{red}}] \cdots} \right)$$

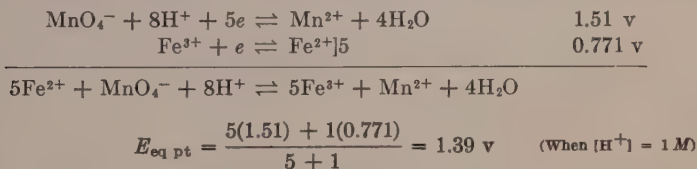
\uparrow This product is unity, from Eqs. *e*.

$$E_{\text{eq pt}} = \frac{\alpha E_A^\circ + \beta E_B^\circ}{\alpha + \beta} \quad (g)$$

Note that when $\alpha = \beta = 1$, as in the Fe(II)-Ce(IV) titration, the equivalence-point E is $(E_A^\circ + E_B^\circ)/2$, as stated on page 444.

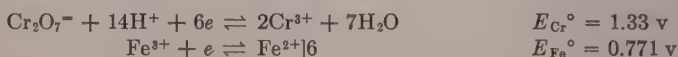
Equation *g* has limitations, and holds only (1) for a chemical equation of the type shown, (2) when there is no product A_{red} or B_{ox} in the system before the titration is begun, and (3) when all species in the chemical equation other than A and B are at unit activities at the equivalence point.

Equation *g* may be applied to the titration of Fe(II) with permanganate to show that the equivalence-point E is much closer to E_{Mn° than to E_{Fe° .



There are types of titrations for which the simple expression of the previous example does not hold. If species other than the oxidized and reduced ones are involved in the half-reactions, E at the equivalence point is of course dependent upon the concentrations of these species. Thus, the equivalence-point potential is *pH*-dependent in many titrations. Sometimes, as shown in the following example, E at the equivalence point may depend upon the initial concentrations of the titrated species. Lingane (112) describes the Ce(IV)- I^- titration, which involves the complexation and precipitation of some of the species. A more general expression for E at the equivalence point has been derived recently (B2).

Example S2. Calculate the equivalence-point E when $C N$ FeSO_4 is titrated with $C N$ $\text{K}_2\text{Cr}_2\text{O}_7$. Assume that (1) activity effects are negligible, (2) volumes are additive, (3) $[\text{H}^+] = h M$ at the equivalence point, and (4) $\text{H}_2\text{Cr}_2\text{O}_7$ is a strong acid.



The equilibrium constant K may be calculated for this reaction by the method of Sec. 19D.3 (p. 410).

$$\begin{aligned} E_{\text{Fe}}^\circ + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} &= E_{\text{Cr}}^\circ + \frac{0.0591}{6} \log \frac{[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}{[\text{Cr}^{3+}]^2} \\ \log \frac{[\text{Fe}^{3+}]^6[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^6[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}} &= \frac{6(E_{\text{Cr}}^\circ - E_{\text{Fe}}^\circ)}{0.0591} \\ \frac{[\text{Fe}^{3+}]^6[\text{Cr}^{3+}]^2}{[\text{Fe}^{2+}]^6[\text{Cr}_2\text{O}_7^{2-}][\text{H}^+]^{14}}, \text{ or } K &= 10^{6(1.33-0.771)/0.0591} = 10^{56.8} \end{aligned}$$

The composition at the equivalence point may be calculated:

From the magnitude of K , it may be seen that Fe is practically completely oxidized to Fe^{3+} at the equivalence point. Hence one unit volume of the original $C N$ Fe^{2+} gives two volumes of $C/2 N$ Fe^{3+} at the equivalence point. Since there is 1 eq per mole of Fe^{3+} , $[\text{Fe}^{3+}]$ at the equivalence point is $C/2 M$.

At the equivalence point there must be formed an amount of Cr^{3+} equivalent to the Fe^{3+} formed. Hence $[\text{Cr}^{3+}] = C/2 N$, or $C/6 M$, since there are 3 eq per mole of Cr^{3+} .

$[\text{Fe}^{2+}]$ remaining at the equivalence point must be very small, and may be defined as $x N$, or $x M$. For each equivalent of Fe^{2+} left unoxidized, there must be an equivalent of $\text{Cr}_2\text{O}_7^{2-}$, so that $[\text{Cr}_2\text{O}_7^{2-}] = x N$, or $x/6 M$.

These concentrations may be substituted into the equilibrium-constant expression to give a value for x .

$$K = \frac{(C/2)^6(C/6)^2}{(x)^6(x/6)(h)^{14}}$$

$$x, \text{ or } [\text{Fe}^{2+}] = \frac{1}{2h^2} \sqrt[7]{\frac{C^8}{3K}}$$

The equivalence-point E may now be found.

$$\begin{aligned} E_{\text{eq pt}} &= E_{\text{Fe}}^\circ + \frac{0.0591}{1} \log \frac{[\text{Fe}^{3+}]}{[\text{Fe}^{2+}]} \\ &= E_{\text{Fe}}^\circ + \frac{0.0591}{1} \log \frac{C/2}{\frac{1}{2h^2} \sqrt[7]{\frac{C^8}{3K}}} \end{aligned}$$

Since $\log K = 6(E_{\text{Cr}}^\circ - E_{\text{Fe}}^\circ)/0.0591$, this expression simplifies to

$$E_{\text{eq pt}} = \frac{E_{\text{Fe}}^\circ + 6E_{\text{Cr}}^\circ}{7} - \frac{0.0591}{7} \log \frac{C}{3} + 2(0.0591) \log h$$

The equivalence-point E therefore depends not only upon the E° values, but also slightly upon C , and considerably upon $[H^+]$. Thus it may be calculated that a change of one pH unit causes a 118-mv change in the equivalence-point potential.

Electrodes Used in Potentiometric Titrations

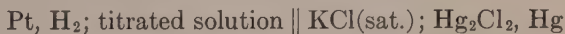
(See Sec. 20B.2a, p. 445)

Indicator electrodes. Any redox titration may be followed potentiometrically, provided that the titrated solution may be converted to a half-cell whose E may be reproducibly taken as a measure of the concentration of either the sought-for or the standard substance. This is done by the immersion of a suitable indicator electrode in the titrated solution. Thus the titration of Fe(II) with dichromate may be followed by the immersion of a Pt electrode in the titrated solution, converting it to a Pt; Fe^{3+} - Fe^{2+} half-cell whose E is a measure of $[Fe^{3+}]/[Fe^{2+}]$.

Any titration not based on a redox reaction may also be followed potentiometrically, provided that there exists a suitable electrode whose E is determined by either the sought-for or the standard substance. Precipitation and pH titrations may be performed potentiometrically, with the indicator electrodes described below. A more rigorous description of these electrodes and others is given in the reference work by Ives and Janz (12).

The hydrogen electrode. The E of any half-cell which involves hydrogen ions may in theory be taken as a measure of $[H^+]$ or pH. There are many such half-reactions, and many indicator electrodes have been devised to follow acid-base titrations potentiometrically. The hydrogen electrode is an example.

Suppose that the following cell is set up.



The hydrogen electrode in the titrated solution may be of the type shown in Fig. 19.4 (p. 418). The calomel electrode may be of the type shown in Fig. 19.5. The voltage, V , of this cell is the difference between the two E 's.

$$V = E_{\text{cal}} - E_H = 0.246 - E_H^\circ - \frac{0.0591}{2} \log \frac{[H^+]^2}{P_{H_2}}$$

If P_{H_2} is maintained at 1 atm, and since $E_H^\circ = 0.00$ v,

$$V = 0.246 - 0.0591 \log [H^+] = 0.246 + (0.0591) \text{ pH}$$

$$\text{pH} = \frac{V - 0.246}{0.0591}$$

The pH is therefore linearly related to the measured V . Thus a plot of V against volume of titrant has the same shape as a pH titration curve, and shows the same sharp rise in the region of the equivalence point.

While the theory of the hydrogen electrode is easy to understand, it is seldom used today for performing titrations or measuring pH . It is not only inconvenient to use, but possesses definite limitations. (1) Even with the platinized surface, several minutes are required to reach equilibrium. (2) Substances capable of oxidizing hydrogen must not be present. While many oxidants do not normally react with hydrogen gas at room temperature, such reaction may be catalyzed at the platinized electrode surface. Examples of such oxidants are $Cu(II)$, $Ag(I)$, $Fe(III)$, and $Cr(VI)$. Such reactions may not only alter the pH of the solution, but may also form deposits on the electrode. In either case, the electrode potential is affected. For similar reasons, strong reductants such as $Cr(II)$ or $Ti(III)$ interfere with pH measurement by the hydrogen electrode. (3) The platinized surface may be poisoned by traces of compounds containing As or S, and by some highly adsorbable organic compounds.

The glass electrode. The glass electrode is different from the redox electrodes described previously, in that the electromotive force is produced by a different mechanism. The glass electrode is a membrane that is selectively permeable only to hydrogen ions—that is, it allows hydrogen ions to diffuse freely, but does not permit the passage of other

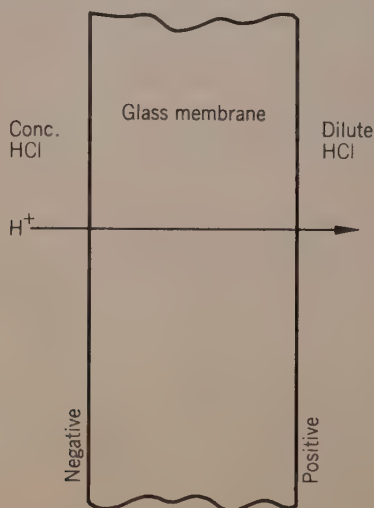


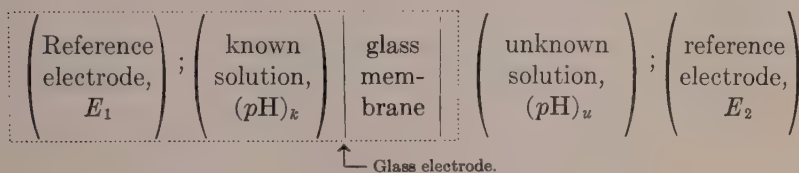
FIG. S20.1. The Potential across a Glass Membrane (Reprinted from H. F. Walton, *Principles and Methods of Chemical Analysis* [Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1952], Fig. 12-6, by permission of the publisher.)

cations or anions. If solutions of different pH are placed on opposite sides of such a membrane, H^+ diffuses from the concentrated to the dilute side. Excess H^+ therefore accumulates in the dilute side, giving it a positive charge with respect to the concentrated side, and giving rise to a potential difference across the membrane, as shown in Fig. S20.1. Ideally, the potential difference set up across the membrane is given by

$$E = 0.0591 \log \frac{[H^+]_{conc.}}{[H^+]_{dilute}}$$

Were the membrane permeable to any cations other than hydrogen ion, E would be dependent upon those cation concentrations as well as on $[H^+]$. Were the membrane equally permeable to anions, such a potential could not arise, for anions would diffuse along with H^+ to keep both sides neutral.

If a glass membrane is used in the following cell, the pH of the unknown solution may be found from the cell voltage, V .



$$V = E_1 + 0.0591 \log \frac{[H^+]_k}{[H^+]_u} - E_2 + E_j$$

$$V = [E_1 - E_2 + E_j - 0.0591 (pH)_k] + 0.0591 (pH)_u$$

E_j is a sum of terms which include junction (p. 446) and asymmetry potentials. An asymmetry potential is one which exists across the glass membrane with identical solutions on each side, and is due to strains in the glass. For a given assembly, the bracketed sum is constant and may be set equal to E' , giving

$$V = E' + 0.0591 (pH)_u$$

V is therefore a linear function of the pH of the unknown solution, and may be taken as a measure of the pH .*

*It should be emphasized that the foregoing equations are only approximations when molar concentrations are used. For exactness, activities should be used, and V should be considered as an exact measurement of pa_H , rather than pH . This statement applies to all electrodes previously discussed. For following titrations, this distinction is of little importance. From the standpoint of precise pH measurements, however, it is of great importance.

In practical measurements, E' is too complicated a term to be calculated theoretically. Instead it is determined experimentally for any given assembly by measuring V for a few buffer solutions of accurately known pH .

The assembly within the dotted box above is called a "glass electrode." A common type of glass electrode is shown schematically in Fig. S20.2. There exist many other types, including electrodes that measure the pH of flowing solutions, and microelectrodes that permit pH measurements on drop-sized samples.

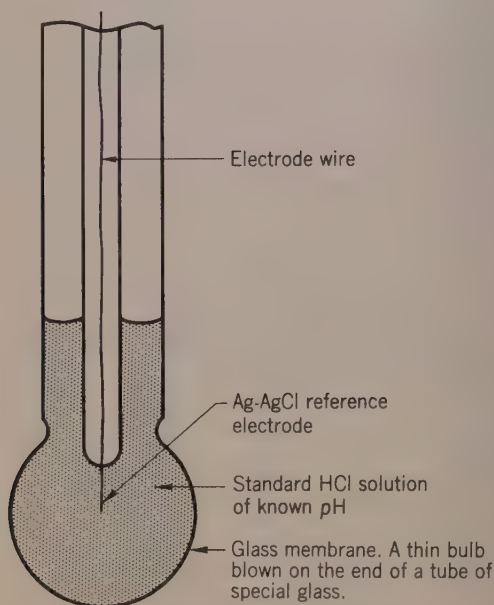


FIG. S20.2. A Glass Electrode

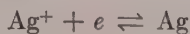
Diffusion through solids is slow, and the membrane must be thin for equilibrium to be reached within a short time. Glass is an insulator, and the membrane must also be thin to avoid high resistance. Even very thin membranes have resistances of 100 megohms, and the ordinary potentiometric method of Fig. 19.6 (p. 419) for measurement of the cell voltage V is inapplicable. V must be measured by a device which draws negligible current, such as a vacuum-tube voltmeter or an electrometer.

At high pH , $[H^+]$ is so low that the diffusion of other cations, such as sodium ion, becomes important. V then depends on other variables besides pH , and deviations from the simple linear relationship derived above occur. For ordinary glass electrodes, these deviations are appreciable above pH 10, but are small and may be corrected for, even

up to pH 12–13. Correction charts are furnished with commercial electrodes. Measurements up to pH 14 may be made with electrodes of special glasses, but these have higher resistances than the ordinary glasses. Excellent elementary (W5) and advanced (12) treatments of the glass electrode may be found in the literature.

The glass electrode is used almost exclusively for accurate pH measurements. It has fewer limitations than other electrodes. It is chemically inert, and does not introduce foreign substances into the solutions being measured. Oxidants, reductants, and organic substances do not interfere. Modern pH meters with glass electrodes are simple to operate and may be used for automatic recording and control of pH .

The silver electrode. A bright silver wire immersed in a solution may be used to measure pAg .



$$E = E^\circ + 0.0591 \log [Ag^+] = 0.799 - 0.0591 (pAg)$$

The E of the Ag electrode is linearly dependent upon the pAg of the solution in which the electrode is immersed. The electrode may thus be used to follow potentiometrically the titration of $AgNO_3$ with standard titrants like $NaCl$, or vice versa.

The Ag-AgCl electrode. An Ag wire coated with $AgCl$ has an E which is linearly dependent upon the pCl of the solution in which the electrode is immersed.



$$E = E^\circ + 0.0591 \log \frac{1}{[Cl^-]} = 0.222 + 0.0591 (pCl)$$

The Ag-AgCl electrode may also be used to follow argentimetric titrations. When immersed in a standard solution, it is as convenient a reference electrode as the calomel electrode; thus in 1 M KCl , E is 0.228 v.

The platinum electrode. When the half-reaction does not involve a metal, it is necessary to use an inert metallic electrode. Platinum or gold is usually used for potentiometric titrations. These electrodes come to equilibrium rapidly in reducing systems, but anomalous behavior is sometimes noted in oxidizing systems.

For example, in the titration of $Fe(II)$ with dichromate, the E of a platinum electrode shows a slow drift after each addition of dichromate in the region of the end point and beyond. The net effect is that the end-point volume of standard dichromate is larger when the $Fe(II)$ is titrated with the dichromate than when the dichromate is titrated with the $Fe(II)$.

This behavior is ascribed to the formation of a platinum oxide film on the electrode in the oxidizing solution (R14). The oxide film forms and dissolves slowly as the E of the solution increases or decreases from the oxidation potential of the Pt, which accounts for the drift. The oxide film is reported to act as a barrier to electron transfer in some systems, and to promote the transfer in other systems.

Reference electrodes. For measurement of E of an unknown or indicator electrode, any electrode may serve as a reference electrode, provided that its E does not change throughout the series of measurements. Two commonly used reference electrodes are the normal and saturated calomel electrodes (Fig. 19.5, p. 418). The Ag-AgCl electrode is often used, dipped into a solution of fixed chloride concentration. The inner reference electrode for the glass electrode is usually an Ag-AgCl electrode (Fig. S20.2, p. 830). To prevent changes in composition, reference electrodes are usually connected through a bridge to the unknown solution.

For titrations, it is not necessary that the E of the reference electrode remain strictly constant; it is only important that E does not change greatly compared to the E of the indicator electrode in the region of the equivalence point. Therefore most titrations may be made with indicator and reference electrodes immersed directly in the titrated solution. For example, an Ag-AgCl electrode may be used without a bridge as a reference electrode for the titration of an HCl solution with standard base. $[\text{Cl}^-]$ changes uniformly and at most by a factor of two or three throughout the whole titration, giving a uniform change of only a few hundredths of a volt in the E of the reference Ag-AgCl electrode. This small uniform change does not interfere with the perception of the abrupt change of an indicator glass electrode in the region of the equivalence point; here $[\text{H}^+]$ may change by several powers of 10, and the E by several tenths of a volt.

Similarly, in the precipitation titration of NaCl with standard AgNO_3 , a little HNO_3 may be added, and the glass electrode may then be used as a reference, while the Ag-AgCl electrode is used as an indicator.

It is important that the reference electrode should not contaminate the system being titrated. The calomel electrode with a KCl bridge (Fig. 19.5) could not be used for titrating NaCl with AgNO_3 . However, this electrode could be used if it were connected to the titrated solution with a KNO_3 bridge.

Automatic Titrations

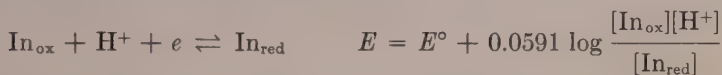
Much attention has been given to making the titration process automatic. The potentiometric method is admirably adaptable to auto-

mation, and many different kinds of equipment are commercially available or are described in the literature (P5). Most instruments stop delivery of titrant when a selected potential is reached. The titrant is delivered automatically from motor-driven syringe-type burets, or from burets with solenoid valves. Some instruments allow the equivalence-point volume to be read from a recorded titration curve. Instruments have been described which automatically stop delivery of titrant at the inflection point. Such automatic instruments are expensive, and require time to set up, adjust, and maintain. Their use is warranted only in continual routine analysis, where they may save considerable time for the worker.

Internal Redox Indicators

(See Sec. 20B.2b, p. 447)

Transition range of a redox indicator. Suppose that an internal redox indicator behaves as follows:



When $[\text{In}_{\text{ox}}] = [\text{In}_{\text{red}}]$, the value of the E is defined as the transition potential, E_t .

$$E_t = E^\circ + 0.0591 \log [\text{H}^+] = E^\circ - 0.0591 (\text{pH})$$

The transition potential is therefore dependent upon pH .

To estimate the magnitude of the transition range, assume, as for acid-base indicators (p. 353), that the oxidized and reduced colors exist respectively when

$$\frac{[\text{In}_{\text{ox}}]}{[\text{In}_{\text{red}}]} \geq 10, \quad \text{and} \quad \frac{[\text{In}_{\text{ox}}]}{[\text{In}_{\text{red}}]} \leq 0.1$$

Then

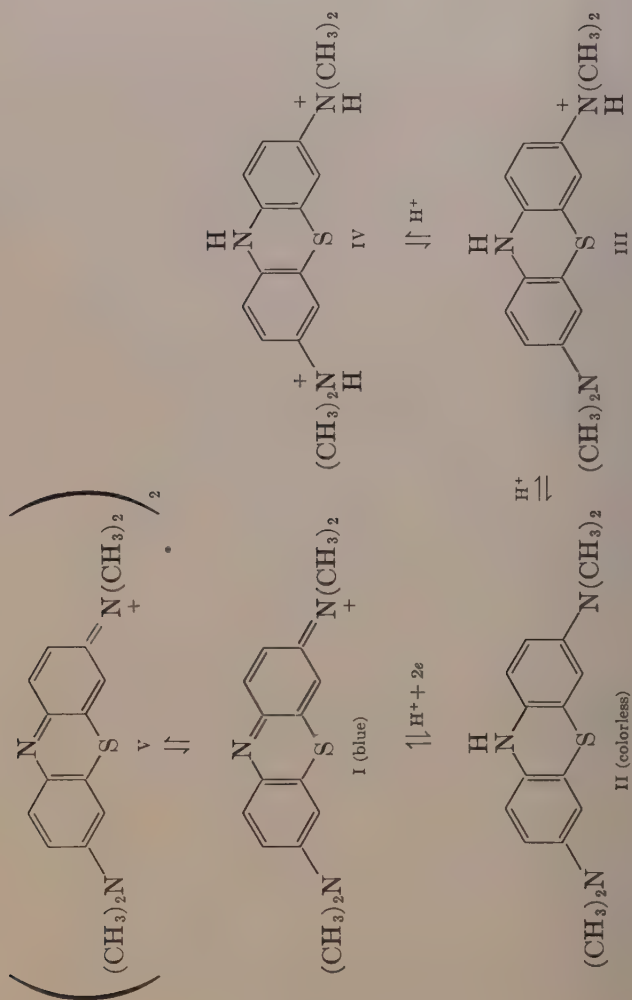
$$E_{\text{ox color}} = E^\circ + 0.0591 \log 10 [\text{H}^+] = E_t + 0.0591$$

$$E_{\text{red color}} = E^\circ + 0.0591 \log 0.1 [\text{H}^+] = E_t - 0.0591$$

The transition from the oxidized to the reduced colors therefore occurs in the range from 0.059 v above the transition potential to 0.059 v below. The magnitude of this indicator's transition range (0.118 v) is independent of pH .

Most indicators do not behave so simply, and the transition potential and range may in some cases depend on the indicator concentration as

well as on pH . An example is methylene blue, whose behavior is represented by the following equilibria (**C3**, **V2**):



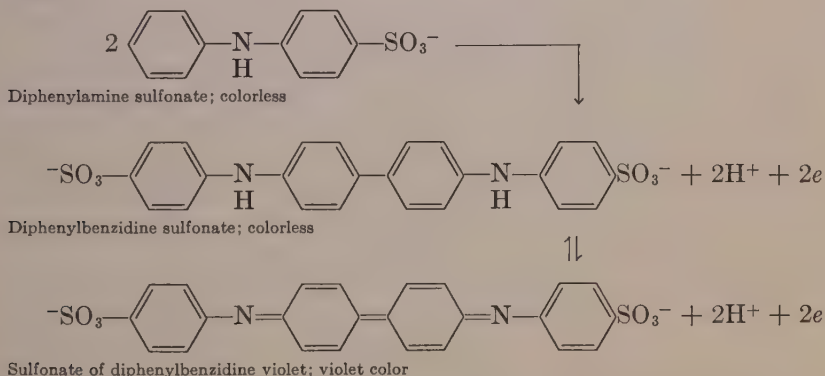
At low pH , form IV is the predominant reduced form, and E shows a third power dependence on $[H^+]$. At high pH , form II is the predominant reduced form, and E shows a linear dependence on $[H^+]$. It has recently been shown that the oxidized form dimerizes, and E is therefore dependent on the total indicator concentration, rather than on just the

ratio of the oxidized and reduced forms. The following expression has been derived for E at low pH .

$$E = E^\circ + 0.0591 \log \frac{[In_{ox}]}{[In_{red}]} + 0.0591 \log [H^+]^3 \frac{\sqrt{1 + 8K[In_{ox}]} - 1}{4K[In_{ox}]}$$

K is the dimerization constant, and $[In_{ox}]$ represents the total (monomer and dimer) indicator in the oxidized form.

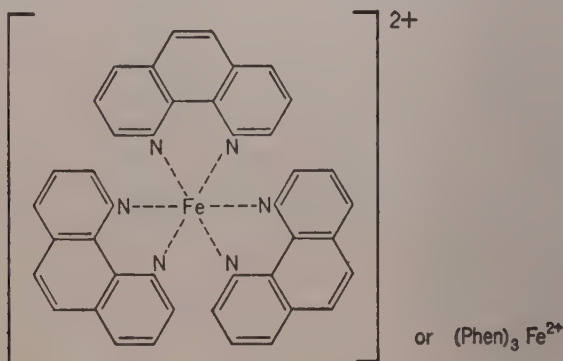
Diphenylamine sulfonic acid. Diphenylamine sulfonic acid is an excellent indicator for many redox titrations. It is available commercially as Na or Ba salts, which are soluble and stable in water. It reacts rapidly in acid solution with $KMnO_4$ and $Ce(SO_4)_2$, but only slowly with $K_2Cr_2O_7$. Fortunately, the reaction with $K_2Cr_2O_7$ is catalyzed by low concentrations of $Fe(II)$, and the indicator may therefore be used conveniently in the $Fe(II)$ -dichromate titration. The mechanism of indicator action involves several steps. First, the diphenylamine sulfonic acid is easily but irreversibly oxidized in acid solution to colorless diphenylbenzidine sulfonate. The colorless sulfonate is then reversibly oxidized in acid solution to the sulfonate of diphenylbenzidine violet, the quinoid structure of this compound being responsible for its color.



The violet form is not indefinitely stable, but undergoes subsequent reactions rather easily, including oxidation to give faintly colored red and yellow products. This causes fading of the end point when excess standard oxidizing agent is added. However, the fading is slow, and the end point is perfectly acceptable. The indicator blank is appreciable, since the indicator reactions given above consume standard oxidizing agent (K19).

Diphenylamine may also be used as an indicator, but it is less soluble than the sulfonic acid derivative.

Ferroin. Orthophenanthroline (1,10-phenanthroline) is an organic compound which forms a very stable and intensely red complex with Fe(II), called *ferroin*.



When oxidized, the faintly blue ferric complex is formed rapidly and reversibly.



The transition potential of ferroin is quite high, and it is an excellent indicator for strongly oxidizing solutions. Ferroin was developed and is used principally for titrations with standard cerate. The Nernst equation describes approximately the behavior of the indicator, since the organic part of the molecule is unaffected in oxidation, and only the oxidation number of the Fe is changed. However, the transition potential is affected by acidity, and the mechanism must involve H^+ , in spite of the apparent simplicity of the above half-reaction.

It would seem that the oxidation of ferroin should be slow. The central Fe^{2+} is completely surrounded by the orthophenanthroline, and an oxidizing agent, such as Ce(IV), cannot penetrate to make actual contact with the central Fe^{2+} . Furthermore, the rate of dissociation of ferroin is low, and exchange does not occur rapidly between Fe^{2+} bound in the complex and Fe^{2+} in solution. Nevertheless, the oxidation of ferroin is rapid. A recent explanation is that the highly conjugated system can conduct the electron from the central Fe^{2+} to the periphery of the complex, where it is available for reaction with the oxidizer, without the oxidizer ever having to come close to the central Fe^{2+} .

Other phenanthrolines and substituted phenanthrolines are also redox indicators, with transition potentials different from ferroin. Nitroferroin is useful for titrations with strong oxidants, since it has a high transition potential.

PERMANGANIMETRIC TITRATIONS

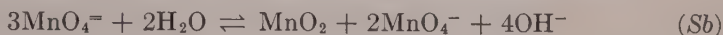
Other Methods of Titration

(See Sec. 20C.1, p. 453)

Titration in basic solution. When permanganate acts as an oxidizer in strongly basic solution, the product is manganate, MnO_4^{2-} .

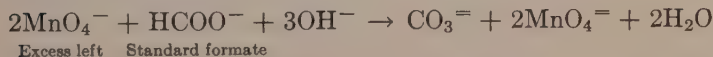
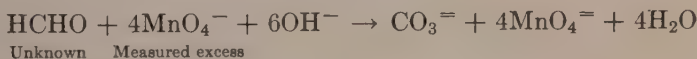


If the solution is not strongly basic, MnO_4^{2-} disproportionates:



Equation *Sa* is a basis for some redox determinations that do not proceed rapidly or completely enough in acid solution.* Among such determinations are: $\text{I}^- \rightarrow \text{IO}_4^-$; $\text{CN}^- \rightarrow \text{CNO}^-$; $\text{S}^{2-} \rightarrow \text{SO}_4^{2-}$; $\text{SO}_3^{2-} \rightarrow \text{SO}_4^{2-}$; and many organic compounds of low molecular weight containing $>\text{C}=\text{C}<$, $\text{C}-\text{OH}$, $\text{C}-\text{NH}_2$, $>\text{C}=\text{O}$, and $-\text{CHO}$, which are oxidized to carbonate. Alkaline permanganate is used principally for the determination of organic substances; other more accurate methods exist for the inorganic substances mentioned above.

To carry out a permanganimetric determination in strongly alkaline solution, the substance is oxidized with excess standard KMnO_4 in 1 *M* NaOH for about 10 minutes at room temperature, or for about 5 minutes at 40°C , but not longer, since permanganate will decompose slowly to MnO_2 . BaCl_2 is added to precipitate BaMnO_4 , thus removing the green manganate, which would obscure the end point. Precipitation of the manganate also prevents its disproportionation (Eq. *Sb*), which would cause error in the titration. The excess permanganate is then titrated with standard sodium formate (HCOONa) in the alkaline solution, a trace of NiNO_3 being used as a catalyst. The end point is the disappearance of the pink color of the excess permanganate. Equations for the determination of formaldehyde are:



Some organic compounds (sugars, polyhydric alcohols, etc.) are not oxidized quantitatively to carbonate, but yield oxalate. In such cases

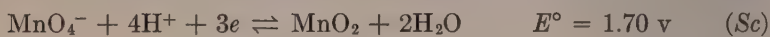
*Some reducers are stronger in neutral or basic solution than in acid solution, and may therefore react more completely in basic solution. Compare $\underline{\text{S}} + 2\text{H}^+ + 2e \rightleftharpoons \text{H}_2\text{S}_{(\text{g})}$ ($E^\circ = 0.14 \text{ v}$) and $\text{S} + 2e \rightleftharpoons \text{S}^{2-}$ ($E^\circ = -0.48 \text{ v}$). Also, the reaction rate may be favored in basic solution.

the solution is acidified and an excess of standard $\text{H}_2\text{C}_2\text{O}_4$ is added sufficient to reduce to Mn(II) all the manganate and permanganate still present. The excess $\text{H}_2\text{C}_2\text{O}_4$ is then titrated in the acid solution with standard KMnO_4 . In this way all the original compound goes to CO_2 , all permanganate goes to Mn(II) , and

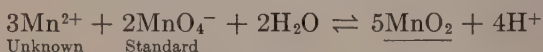
$$\left(\begin{array}{c} \text{eq of} \\ \text{organic} \\ \text{compound} \end{array} \right) = \left(\begin{array}{c} \text{eq of KMnO}_4 \\ \text{added before} \\ \text{oxidation} \end{array} \right) + \left(\begin{array}{c} \text{eq of KMnO}_4 \\ \text{used in} \\ \text{titration} \end{array} \right) - \left(\begin{array}{c} \text{eq of oxalate} \\ \text{added before} \\ \text{titration} \end{array} \right)$$

The error of this procedure is 0.5–1%, its principal source being the decomposition of KMnO_4 in the alkaline solution. This procedure is excellently summarized, with references, by Walton (W5). Periodic acid or cerate in perchloric acid possesses advantages over alkaline permanganate in the determination of organic compounds.

Titrimetric in neutral solution. In weakly acid or weakly basic solution (pH 4–10), permanganate is reduced predominantly to MnO_2 :



The only important titration based on this reaction is the Volhard determination of Mn^{2+} .



The accuracy is not high, and the visual end point is troublesome because of the MnO_2 in the system at the equivalence point. The advantage is that the Mn does not have to be preoxidized before titration, which means, in principle at least, that other preoxidizable elements (like V, Fe, Mo, W, U, etc.) would not interfere.

Titrimetric in the presence of pyrophosphate. In the Lingane-Karplus method (L13), Mn(II) in a sample is titrated with standard permanganate in the presence of pyrophosphate.



Mn(III) is a very strong oxidant, and is not normally an end product of permanganate titrations. However, Mn(III) forms very tight complexes with fluoride and pyrophosphate, and is stabilized by them. The advantage of this procedure over the Volhard titration is that no precipitate is formed. It has been shown that V, Zn, Fe, Cu, Cr, Ni, Co, Mo, W, U, Mg, and Cd do not interfere. The $\text{Mn(III)}-\text{H}_2\text{P}_2\text{O}_7^{4-}$ complex is pink, so the end point must be established potentiometrically. The method has also been used to titrate Hg(I) , Te(IV) , and Se(IV) .

Other Methods of Standardization

(See Sec. 20C.2c, p. 454)

Standardization with $\text{Na}_2\text{C}_2\text{O}_4$. Analyzed reagent-grade $\text{Na}_2\text{C}_2\text{O}_4$ may be used as a primary standard without further purification. The assay value is well over 99.9% $\text{Na}_2\text{C}_2\text{O}_4$, and it is stable and easily dried. $\text{Na}_2\text{C}_2\text{O}_4$ solutions are not stable when stored for long periods in glass vessels, since the glass is attacked. The stability of $\text{Na}_2\text{C}_2\text{O}_4$ solutions in polyethylene bottles has not yet been reported.

The stoichiometrical reaction for the oxidation of oxalate by permanganate in acid solution is



The reaction tendency between permanganate and oxalate in acid solution is great, but the rate is low at room temperature. This may be proved by noting the persistence of the KMnO_4 color, even at 60–90°C, when the first few drops of standard KMnO_4 are added to an excess of $\text{H}_2\text{C}_2\text{O}_4$. After a little while, however, the color disappears. Addition of another small portion of KMnO_4 gives much faster decolorization. This indicates that the reaction is catalyzed by one of its products (i.e., autocatalyzed). Actually, the reaction is a very complicated one, proceeding stepwise through many reactions. Unless titration conditions are very carefully controlled, side reactions may occur at some of these steps to destroy the stoichiometry of the reaction. Two of the main causes of error are the decomposition of KMnO_4 in the warm solution, and the induced oxidation of $\text{C}_2\text{O}_4^{2-}$ by air:

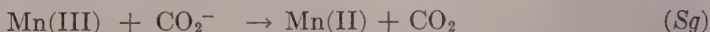


These two errors are opposite in sign, and tend to cancel, so that properly selected titration conditions give errors not exceeding a few parts per thousand.

Reaction *Sb* by itself causes no error because the H_2O_2 reacts with the same amount of permanganate as the $\text{C}_2\text{O}_4^{2-}$ from which the H_2O_2 came. The error arises because some of the H_2O_2 decomposes by itself and some escapes from the hot solution.

The MnO_4^- - $\text{C}_2\text{O}_4^{2-}$ reaction has been studied since the turn of the century, and the following catalytic mechanism is a simplified version of one (A1) of several that have been proposed.





When Mn(II) is low, as at the beginning of the titration, the rate is low. If Mn(II) is present, then it can catalyze the reaction between Mn(VII) and C_2O_4^- via steps *Sc-Sg*, the sum of which gives the over-all stoichiometric reaction *Sa*. In the presence of air, oxygen competes with Mn(III) for the CO_2^- , leading to the induced chain *Sh*, *Si*, and *Sf*:



The induced oxidation is favored at the beginning of the titration, when Mn(II) is low.

In the McBride procedure (**M1**) an attempt is made to achieve stoichiometric reaction by slow titration at an intermediate temperature (60–90°C). This temperature is high enough to give rapid oxidation of $\text{H}_2\text{C}_2\text{O}_4$ by KMnO_4 , but not high enough to permit excessive decomposition of KMnO_4 or of $\text{H}_2\text{C}_2\text{O}_4$. It has been shown that the McBride method requires a few tenths of a per cent less than the stoichiometric amount of KMnO_4 , primarily because of decomposition of $\text{H}_2\text{C}_2\text{O}_4$. Fowler and Bright (**F8**) describe a more accurate procedure, in which the bulk (90–95%) of the standard KMnO_4 is added to the $\text{H}_2\text{C}_2\text{O}_4$ at 25–30°C. The mixture is allowed to stand until the color disappears ($\frac{1}{2}$ –1 minute). The solution is then heated to 55–60°C and the titration is completed. By performing the greater part of the titration at low temperature and in the presence of excess KMnO_4 , decomposition of $\text{H}_2\text{C}_2\text{O}_4$ and loss of H_2O_2 are minimized. However, the concentration of the KMnO_4 to be standardized must be known rather closely before the Fowler and Bright method may be used. In practice, it is recommended that the first of a series of replicate determinations be made by the McBride method, to find the approximate composition of the sample, and that subsequent determinations be made by the more exact procedure of Fowler and Bright. The techniques are described in Exp. 20.2.

It has recently been demonstrated that a mixture of Mn^{2+} and another metal ion (like Cu^{2+} , Zn^{2+} , etc.) catalyzes the reaction sufficiently to permit the titration at 25°C (**I1**). If chloride is present, its oxidation by MnO_4^- is induced by the MnO_4^- - C_2O_4^- reaction, but the mechanism has not yet been worked out (**D10**, p. 656).

Standardization with KI. Ordinary reagent-grade KI contains KIO_3 , which causes error. The error can be eliminated by running a blank. In fairly concentrated HCl solution (4 *M*), iodide is oxidized through free iodine to ICl by permanganate.



As the iodide is titrated with the permanganate, iodine first forms and then disappears as the ICl equivalence point is approached. The end point may be determined potentiometrically or by the extraction method. Starch indicator cannot be used.

Example. What is the normality of a KMnO_4 solution, if 25.00 ml are required to titrate a 0.2000-g sample of KI by the foregoing method?

Equivalent weight of KI is $166.01/2$, or 83.005.

$$\frac{200.0}{83.005} \times \frac{1}{25.00} = 0.0964 \text{ N}$$

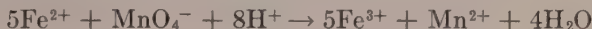
meq KMnO_4 per ml

meq KI = meq KMnO_4 in 25.00 ml

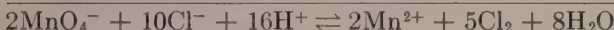
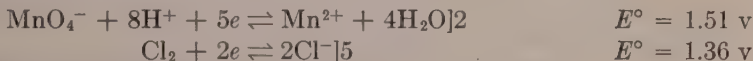
Permanganimetric Determination of Iron

(See Exp. 20.1, p. 476)

The titration of Fe(II) with permanganate proceeds smoothly and stoichiometrically in H_2SO_4 or HClO_4 solution.



However, if chloride is present there may be error due to oxidation of chloride by permanganate.

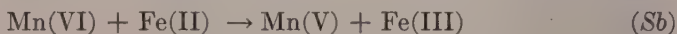


Usually, if $[\text{Cl}^-]$ is less than 1 M , the rate of oxidation of chloride by permanganate is too low to cause error. Thus $\text{H}_2\text{C}_2\text{O}_4$ and H_3AsO_3 may each be titrated with KMnO_4 in the presence of chloride without significant error. The presence of Fe(II), however, induces the oxidation of Cl^- by MnO_4^- , and the odor of chlorine is noted long before the equivalence point is reached. Were it all reduced by Fe^{2+} , the intermediate formation of chlorine would cause no error; the error is caused by that part of the chlorine that escapes from the solution. If the induced oxidation of Cl^- is not inhibited, the amount of MnO_4^- consumed may be too large by several per cent.

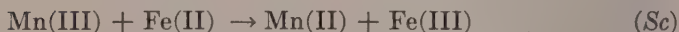
Laitinen gives a critical discussion of various mechanisms that have been proposed (L2). The following is essentially that proposed by Kolthoff (K18), with some modifications.

If only Fe(II) and MnO_4^- are present in the system, the oxidation must proceed through intermediate oxidation states of Mn. Since an Fe(II) can donate only one electron, the oxidation number of Mn can

be reduced by only one step at a time, and intermediate oxidation states of Mn might be present during the reaction:



.
.
.



If uncomplexed, these intermediate oxidation states of Mn are strong oxidizers, readily capable of oxidizing Cl^- to chlorine. If Cl^- is present, it will compete with Fe(II) in Eqs. Sb–Sc for the intermediate oxidation states of Mn, and the oxidation of Cl^- is thereby induced.

The induced oxidation of Cl^- is inhibited by Zimmermann-Reinhardt *preventive solution*. This solution contains Mn^{2+} , which also reacts with the intermediate oxidation states of Mn (see Eqs. Sd and Se, p. 839), to keep their concentrations low, and thus to reduce their rate of reaction with Cl^- . Preventive solution also contains H_3PO_4 , which is known to complex strongly with Mn(III),* reducing its oxidizing power to such an extent that it no longer readily oxidizes Cl^- .

The H_3PO_4 in preventive solution incidentally forms stable and colorless Fe(III)-PO_4^- complexes, removing the rather intense yellow color of FeCl_3 and other Fe(III)-chloride complexes, which would otherwise obscure the delicate pink permanganate end point.

In the presence of Cl^- , Fe(II) can be titrated more accurately and simply with cerate or dichromate than with permanganate, since the induced oxidation of Cl^- does not occur.

IODIMETRIC TITRATIONS

Titration Based on Higher Oxidation States of Iodine

(See Sec. 20D.1, p. 458)

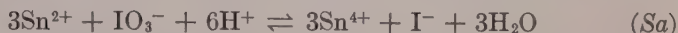
Iodine may exist in several oxidation states, each being very stable under certain conditions. Good titration procedures exist that are based on these higher oxidation states, and while not so widely used as iodimetric methods, they are extremely useful in particular applications.

Titration with KIO_3 . Analyzed reagent-grade KIO_3 that has been dried for 2 hours at 120°C has an assay value above 99.9%, and may be

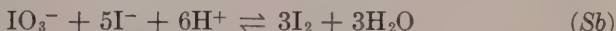
* E° for the $\text{Mn}^{3+}\text{-Mn}^{2+}$ half-reaction is about 1.5 v, but in the presence of pyrophosphate, the formal E is only about 1.15 v (L2, p. 360). Other complexers, like F^- , PO_4^{3-} , acetate, etc., behave similarly.

used as a primary standard to prepare stable standard solutions. Standard KIO_3 is a versatile oxidant when used under certain conditions, for it may be made to go quantitatively to any of several lower oxidation states ($-1, 0, +1$).

When standard KIO_3 solution is titrated into a moderately acid solution ($0.1\text{--}1\text{ }M\text{ HCl}$) containing a moderately strong reducing agent, the KIO_3 is initially reduced to iodide, since the reductant is in excess.

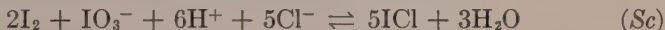


The first slight excess of KIO_3 titrant added past the equivalence point gives an end point marked by the appearance of iodine and detectable with starch.



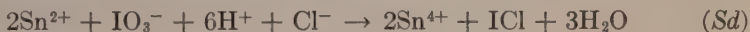
There are 6 eq per mole of KIO_3 in this determination.

In practice, however, most titrations with KIO_3 are carried to the iodine monochloride (ICl) end point. In strongly acidic solution ($4\text{--}6\text{ }M\text{ HCl}$), iodate can oxidize not only iodide, but also iodine, to ICl .^{*} Thus even though iodide and iodine might be formed in the initial stages of titration, the iodine is oxidized to ICl if the titration is continued.



The equivalence point in this titration is marked by the disappearance of the last trace of the iodine color. Starch is not a suitable indicator, and the extraction end point is most often used. Several irreversible color indicators have been described for this reaction (**S21**).

In strongly acid solution, then, the over-all reaction for the determination of Sn(II) with standard KIO_3 to the ICl end point is



There are 4 eq per mole of KIO_3 in this determination.

Table S20.2 lists some substances determinable with KIO_3 . Directions for these titrations may be found in several texts (**J2**, **K19**).

There is one unique advantage of performing the KIO_3 titration to the ICl end point rather than to the iodine end point: reducing substances may be determined that are too weak to reduce iodate quantitatively

^{*}The oxidation state of iodine is $+1$ in ICl . This state is not stable as I^+ in acid solutions, but forms stable complexes such as ICl , IBr , and ICN . These complexes are stable only at high acidity; if the acidity is not high, reaction *Sc* is incomplete. The ICN complex is more stable than ICl , so that titrations with KIO_3 may be carried out in the presence of HCN at lower acid concentration ($1\text{--}2\text{ }M\text{ HCl}$). This is a slight advantage, since starch may be used at this acidity. Because of the toxicity of HCN , the method is not recommended for routine use.

TABLE S20.2

IODATE TITRATIONS

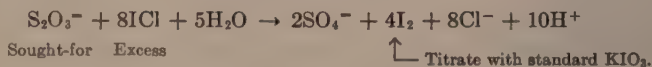
A. DIRECT TITRATIONS

Substance	Comments
$\text{H}_3\text{AsO}_3 \rightarrow \text{H}_3\text{AsO}_4$	
$\text{H}_3\text{SbO}_3 \rightarrow \text{H}_3\text{SbO}_4$	
$\text{Sn}^{2+} \rightarrow \text{Sn}^{4+}$	
$\text{Tl}^+ \rightarrow \text{Tl}^{3+}$	
$^*\text{S}_2\text{O}_3^{=}\rightarrow \text{SO}_4^{=}$	
$^*\text{S}_4\text{O}_6^{=}\rightarrow \text{SO}_4^{=}$	
$^*\text{SO}_3^{=}\rightarrow \text{SO}_4^{=}$	
$^*\text{SCN}^- + 4\text{H}_2\text{O} \rightarrow$ $\text{CN}^- + \text{SO}_4^{=} + 8\text{H}^+ + 6e$	
$\text{I}^- \rightarrow \text{ICl}$	
$\text{I}_2 \rightarrow \text{ICl}$	
$\text{Br}^- \rightarrow \text{BrCl}$	No interference by Cl^- .
$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4 \rightarrow$ $\text{N}_2 + \text{SO}_4^{=} + 6\text{H}^+ + 4e$	
$\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$	No interference by V.
$\text{Mo}^{3+} \rightarrow \text{MoO}_2^+$	Prereducd Mo with Zn reductor.
<u>$\text{Hg}_2\text{Cl}_2 \rightarrow \text{HgCl}_2$</u>	Applicable to determination of Hg_2Cl_2 in medicinals, without prior removal of many organic substances.

B. INDIRECT TITRATIONS

Cu^{2+}	Reduce Cu^{2+} with SO_2 . Precipitate and isolate CuSCN . Dissolve in HCl and titrate thiocyanate as above.
Hg_2^{2+} (Also Zn^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+}) H_2O_2	Precipitate and isolate $\text{HgZn}(\text{SCN})_4$. Dissolve in HCl and titrate thiocyanate as above. Add excess standard Na_3AsO_3 , and determine excess as above.
$\left. \begin{array}{l} \text{PbO}_2, \text{MnO}_2 \\ \text{K}_2\text{Cr}_2\text{O}_7 \\ \text{KMnO}_4 \\ \text{KClO}_3 \end{array} \right\}$ $\text{VO}_2^+ \rightarrow \text{VO}^{2+}$	Add excess standard KI , which in strong HCl is oxidized to iodine by these oxidants. Titrate excess KI remaining (and iodine formed) as above.

* These substances are not very stable in acid solution, and the following indirect method is often used. The sought-for reducer is added to an acidified solution of ICl , reducing the ICl to iodine. The iodine formed is determined by titration with standard KIO_3 .



The ICl added need not be a standard solution. It is prepared by adding KIO_3 to KI in 6 M HCl until the extraction end point just shows the disappearance of the iodine color (S36). The sample is then added, reaction occurs, and the iodine formed is titrated back to ICl with standard KIO_3 . This indirect method is also used for reductants, such as Fe(II) or Mo(III), that might be slowly oxidized by air during the relatively slow direct titration with standard KIO_3 .

to iodide or iodine, but that are strong enough to reduce iodate quantitatively to ICl. Such substances are iodide, iodine, and Fe(II).

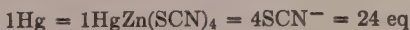
Being a weaker oxidizing agent than KMnO_4 or cerate, KIO_3 is often more selective. Interfering substances that would reduce stronger oxidants need not always be removed when standard KIO_3 is used; thus time and effort may be saved in sample preparation. Titrations may be made with KIO_3 in the presence of organic matter (filter paper, alcohol, citric and tartaric acids, etc.). Also, Fe(II) may be determined without interference by V, and bromide may be determined in the presence of chloride.

Example S1. What weight of Mo is in a sample which requires 20.25 ml of 0.1000 N KIO_3 for titration according to the method of Table S20.2A? (Normality of the KIO_3 solution is with respect to reduction to ICl, and 0.1 N is 0.025 M .)

$$0.1000 \times 20.25 \left| \begin{array}{l} \times \frac{95.94}{2} \\ \text{mg Mo} \\ \text{--- meq KIO}_3 = \text{meq Mo} \end{array} \right| = 97.1 \text{ mg Mo}$$

Example S2. What is the weight of Hg in a sample which requires 26.25 ml of 0.1000 N KIO_3 for titration by the method of Table S20.2B? (Normality of KIO_3 is with respect to reduction to ICl, and 0.1 N is 0.025 M .)

To find the equivalent weight of Hg,



$$0.1000 \times 26.25 \left| \begin{array}{l} \times \frac{200.59}{24} \\ \text{mg Hg} \\ \text{--- meq KIO}_3 = \text{meq of thiocyanate} = \text{meq Hg} \end{array} \right| = 21.94 \text{ mg Hg}$$

The iodate-iodide reaction. In acid solution, KI and KIO_3 react, the iodide being oxidized to iodine, and the iodate being reduced to iodine if iodide is in excess.



Procedures for determining iodate, thiosulfate, and acid are based on this useful reaction.

To determine iodate in a sample, excesses of KI and of acid are added. The iodine formed is equivalent to the sought-for iodate, and may be determined by titration with standard $\text{Na}_2\text{S}_2\text{O}_3$ to the starch end point. In this reaction, there are six (not five) redox equivalents per mole of KIO_3 (see Ex. 2, p. 466). $\text{Na}_2\text{S}_2\text{O}_3$ solutions may be standardized in similar manner, a known amount of KIO_3 being used as a primary standard.

Acid solutions may be standardized as follows (S36). A measured amount of primary standard KIO_3 is dissolved in pure water. To this solution are added excesses of KI and of $\text{Na}_2\text{S}_2\text{O}_3$, and a few drops of methyl red or methyl orange indicator. No reaction takes place between iodate and iodide as long as the pH is 6 or greater. After the acid to be standardized is added, it is used according to the foregoing equation, and liberates iodine, which immediately reacts with the $\text{Na}_2\text{S}_2\text{O}_3$ and leaves a clear solution. All the acid added is used in this way until the KIO_3 is gone; then the first slight excess of acid past the KIO_3 equivalence point survives and changes the indicator color. In this standardization, 1 mole of iodate is equivalent to 6 moles of H^+ . In general, weak acids cannot be so determined; since the end point is around pH 6, part of the weak acid remains undissociated at the end point, which gives low results. It is for this reason also that standard HCl cannot be used to standardize $\text{Na}_2\text{S}_2\text{O}_3$ solutions containing preservatives such as Na_2CO_3 or borax.

Example S3. A 0.2500-g sample of KIO_3 is used to standardize an HCl solution by the procedure above. What is the normality of the acid solution if 46.72 ml are required for titration?

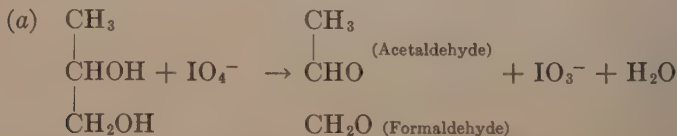
$$1\text{KIO}_3 = 6\text{HCl}$$

$$\frac{250.0}{214.00} \times 6 \times \frac{1}{46.72} = 0.1500 \text{ N HCl}$$

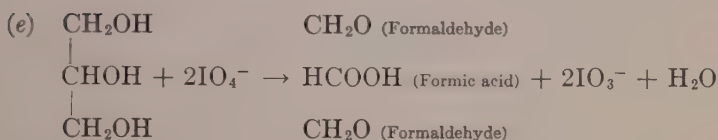
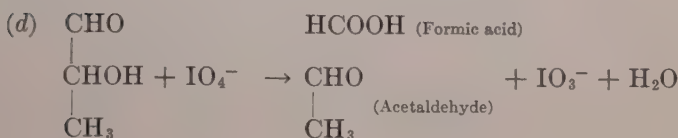
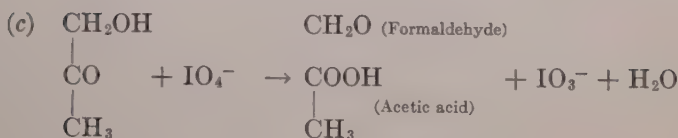
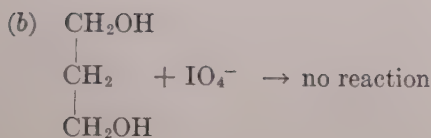
$\underbrace{\hspace{10em}}_{\text{mmoles H}^+ \text{ in 46.72 ml}}$
 $\underbrace{\hspace{10em}}_{\text{mmoles H}^+ \text{ in 46.72 ml}}$
 $\underbrace{\hspace{10em}}_{\text{mmoles KIO}_3 \text{ in sample used}}$

Periodic acid. Periodic acid* (HIO_4 or H_5IO_6) or an acid solution of KIO_4 is used principally as a preoxidant.

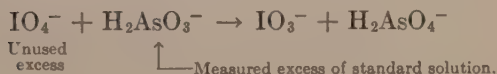
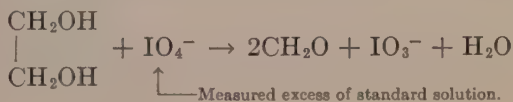
However, periodate is very useful in the quantitative determination of certain types of organic compounds. In approximately neutral solution, periodate selectively splits $\text{C}-\text{C}$ bonds in compounds having $-\text{OH}$, $=\text{O}$, or $-\text{NH}_2$ on adjacent carbon atoms, $\text{C}-\text{OH}$ yielding CHO , $\text{C}=\text{O}$ yielding COOH , and $\text{C}-\text{NH}_2$ yielding CHO (and NH_3). One IO_4^- is used per $\text{C}-\text{C}$ bond that is split. The following five examples serve to illustrate the nature of the cleavage, which is called the *Malaprade reaction*, after its originator.



*Some authors give the formula as HIO_4 . From the state of periodic acid in solution, the formula should more properly be given as H_5IO_6 (S21).



The cleavage is performed in weakly acid, neutral, or weakly basic solution—an NaHCO_3 solution is suitable. A measured excess of standard periodate solution is added to the compound, and the reaction is made to occur, usually at or below room temperature. (Elevated temperature hastens the reaction, but also promotes error-causing side reactions.) After reaction, the remaining periodate is determined by adding an excess of standard Na_3AsO_3 in neutral or weakly basic solution, where IO_4^- is reduced to stable IO_3^- . The remaining arsenite is titrated with standard iodine solution. Equations for the determination of ethylene glycol follow.



The Malaprade reaction has many analytical uses, both qualitative and quantitative. If a sample contains only one known compound,

simple measurement of the IO_4^- consumed gives the amount of that compound. If a mixture is present, the IO_4^- consumed gives only the total equivalents of substances that are cleavable by periodate. However, methods exist for the estimation and identification of the other cleavage products, such as formaldehyde, formic acid, NH_3 , and other aldehydes, ketones, and acids. Such data permit both the identification and estimation of a single compound in a sample (see example below), or the analysis of simple mixtures. The periodate reaction has been of great use in the determination of structure in organic compounds.

Standard periodate solutions may be prepared from reagent-grade periodic acid and then standardized, or from KIO_4 as a primary standard.

There are exceptions to the above general statements that can be found in more detailed treatments (K19). For example, if the time is too long or if the temperature is too high, further oxidation of the cleavage products occurs, and so does oxidation of groupings other than those described above. In fact, side reactions are usually present even under optimum conditions, and errors are of the order of several per cent.

Example. A 1.000-g sample containing a single organic compound and inert materials was treated with 25.00 ml of 0.3200 M KIO_4 . After reaction, semiquantitative analysis gave glyoxylic acid ($\text{HOOC}\cdot\text{CHO}$) and acetaldehyde ($\text{H}_3\text{C}\cdot\text{CHO}$) in approximately equimolar amounts as the only cleavage products. A 50.00-ml aliquot of 0.1000 M Na_3AsO_3 was added to the reaction mixture, after which 40.00 ml of 0.1000 N iodine were required for titration. Tell what the compound is, and calculate the percentage of it in the sample.

The only possible molecule that can yield glyoxylic acid and acetaldehyde in equimolar amounts is α,β -dihydroxybutyric acid ($\text{H}_3\text{C}\cdot\text{CHOH}\cdot\text{CHOH}\cdot\text{COOH}$). Sometimes, the choice is not so clear, and additional evidence must be obtained in order to identify the compound.

Knowing the compound, and knowing that each mole of periodate used represents one mole of the compound, its percentage in the original sample may be calculated.

$$\begin{aligned} \left(\begin{array}{c} \text{mmoles per-} \\ \text{iodate used} \end{array} \right) &= 25.00(0.3200) - [50.00(0.1000) - 40.00(0.1000)/2] \\ &\quad \uparrow \begin{array}{c} \text{mmoles periodate left after cleavage} \\ \text{Total mmoles periodate added.} \end{array} \\ &= 5.00 \end{aligned}$$

$$\left(\begin{array}{c} \text{Percentage of } \alpha,\beta\text{-} \\ \text{dihydroxybutyric acid} \end{array} \right) = 5.00 \times 120.11 \times \frac{100}{1000} = 60.1\%$$

There are a few quantitative inorganic applications of periodate. For instance, K is precipitated quantitatively as KIO_4 by excess periodic acid in water-alcohol solutions. The K may be determined by weighing

the KIO_4 , or indirectly by redissolving the KIO_4 in water and titrating the periodate iodimetrically.

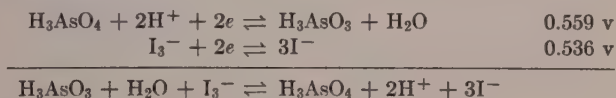
Titration with ICl or hypohalites. Titrations have been reported with standard solutions of ICl , BrCl , NaOCl , and NaOBr , but they do not possess significant advantages over the more frequently used standard solutions.

Completeness of the Iodine-Arsenite Reaction

(See Sec. 20D.3a, p. 460)

Example. Calculate the equilibrium constant of the iodine-arsenite reaction (p. 461), and calculate the pH which must exist at the equivalence point in order that the titration of $0.0500\text{ }M\text{ H}_3\text{AsO}_3$ with $0.0500\text{ }M\text{ I}_2$ will be at least 99.99% complete. Neglect all activity effects. Assume also that the iodine solution contains no KI .

It must be recognized that there is a large excess of I^- at the end point, since iodine is quantitatively reduced. Hence any remaining iodine exists predominantly as I_3^- , and the reaction is



At equilibrium, $E_1 = E_{\text{As}}$, by the method on page 410, and

$$0.536 + \frac{0.0591}{2} \log \frac{[\text{I}_3^-]}{[\text{I}^-]^3} = 0.559 + \frac{0.0591}{2} \log \frac{[\text{H}_3\text{AsO}_4][\text{H}^+]^2}{[\text{H}_3\text{AsO}_3]}$$

$$\frac{[\text{H}_3\text{AsO}_4][\text{H}^+]^2[\text{I}^-]^3}{[\text{H}_3\text{AsO}_3][\text{I}_3^-]} = \text{antilog} \frac{2(-0.023)}{0.0591} = 0.17$$

If the reaction is 99.99% complete at the equivalence point, practically all of the original H_3AsO_3 is oxidized to H_3AsO_4 , and $[\text{H}_3\text{AsO}_4] = 0.0500/2 = 0.0250\text{ }M$. (The volume of the original H_3AsO_3 solution is doubled by adding an equivalent volume of iodine solution.) Similarly, practically all of the original iodine must be reduced to iodide, and $[\text{I}^-]$ at the equivalence point must be $2(0.0500)/2$, or $0.0500\text{ }M$.

If 0.01% of the total As remains unoxidized, $[\text{H}_3\text{AsO}_3]$ at the equivalence point is 0.0001×0.0250 , or $2.5 \times 10^{-6}\text{ }M$. Similarly, if 0.01% of the iodine remains un-reduced, $[\text{I}_3^-]$ must be $2.5 \times 10^{-6}\text{ }M$.

These concentrations may be substituted into the equilibrium-constant expression to give an estimate of $[\text{H}^+]$.

$$\frac{(0.02500)[\text{H}^+]^2(0.05000)^3}{(2.5 \times 10^{-6})(2.5 \times 10^{-6})} = 0.17$$

$$[\text{H}^+] = \sqrt{3.4 \times 10^{-7}} = 6 \times 10^{-4}$$

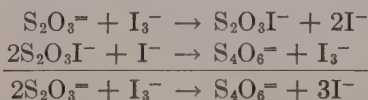
Hence the required pH is above 3. This represents a minimum pH (i.e., maximum acidity) if the reaction is to be at least 99.99% complete.

Note the large (cubed) effect that $[\text{I}^-]$ has in the mass-action expression, which emphasizes the importance of keeping $[\text{I}^-]$ low in order to promote complete reaction.

Mechanism of the Iodine-Thiosulfate Reaction

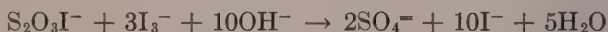
(See Sec. 20D.4a, p. 463)

In the presence of excess I^- , the following has been proposed (A16).



The desired stoichiometric reaction is favored by a high I^- concentration.

At high $p\text{H}$, the oxidation of $\text{S}_2\text{O}_3^{2-}$ to SO_4^{2-} may occur as a side reaction, causing error:

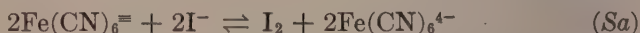
**Standardization of $\text{Na}_2\text{S}_2\text{O}_3$ with $\text{K}_3\text{Fe}(\text{CN})_6$ (S36)**

(See Sec. 20D.4b, p. 464)

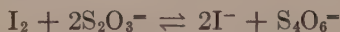
The indirect standardization of $\text{Na}_2\text{S}_2\text{O}_3$ with $\text{K}_3\text{Fe}(\text{CN})_6$ is not widely used, but is included here because of the instructive equilibrium principles involved.

$\text{K}_3\text{Fe}(\text{CN})_6$ may be easily prepared as a primary standard substance. If the reagent-grade material has an assay value, it is sufficient to powder and dry it for only an hour or two at $100\text{--}110^\circ\text{C}$, at which temperature there is no decomposition. If no assay value accompanies the material, a single recrystallization from water gives a very pure preparation, which may then be dried.

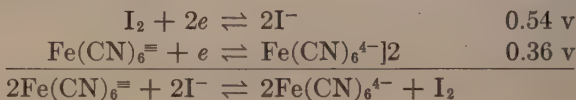
The standardization procedure is an indirect one: a known amount of $\text{K}_3\text{Fe}(\text{CN})_6$ is added to an excess of KI acidified with HCl , liberating iodine.



The iodine is titrated with $\text{Na}_2\text{S}_2\text{O}_3$, after an excess of ZnSO_4 is added to precipitate zinc ferrocyanide and to drive reaction *Sa* to the right.

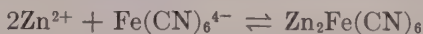


The reaction between ferricyanide and iodide is not complete, according to the TSP.



Actually, the E of the ferricyanide-ferrocyanide half-reaction is greater than 0.36 v in acid solution, since ferrocyanic acid is much weaker than ferricyanic acid. In 0.1 M HCl the E is 0.56 v . Even at this acidity

the oxidation of iodide by ferricyanide is incomplete. However, two other circumstances contribute to give complete oxidation of iodide by ferricyanide. First, zinc ferrocyanide is insoluble, whereas zinc ferricyanide is soluble. Hence the addition of Zn(II) to the system raises the E of the ferricyanide-ferrocyanide half-reaction even more, and forces reaction *Sa* to the right by removing ferrocyanide.*



Second, when the iodine is titrated with $\text{Na}_2\text{S}_2\text{O}_3$, iodine is effectively removed from the system, lowering the E of the iodine-iodide half-reaction and forcing reaction *Sa* to the right. In sum, all these measures combine to make the oxidation of iodide by ferricyanide quantitative.

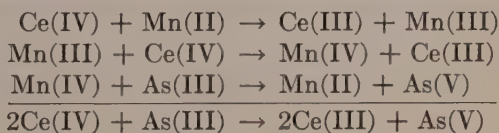
CERATE TITRATIONS

The Ce(IV)-As(III) Reaction

(See Sec. 20E.2, p. 469)

The major part of the titration may be performed at room temperature, but the rate slows as the end point is approached, and the titration must be completed at 50°C. A moderately high concentration of ICl is required (about $10^{-4} M$), and the blank would be appreciable if the iodine were introduced in any form other than ICl, the state to which iodine is oxidized by Ce(IV) at the end point. The procedure for preparation of the ICl catalyst is described on page 844.

The slowness of the uncatalyzed reaction between Ce(IV) and As(III) is probably due to its termolecular nature. Mn(II) may catalyze the process by making a bimolecular mechanism possible (M21).

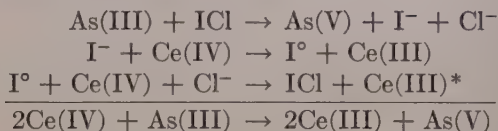


Iodine catalyzes the Ce(IV)-As(III) reaction with phenomenal effectiveness. A system that contains 0.025 *N* Ce(IV), 0.025 *N* H_3AsO_3 , and 1.5 *N* H_2SO_4 requires 36 hours for complete reaction in the absence of iodine. In the presence of $10^{-5} M \text{I}^-$, reaction is complete within a minute (K16).

The kinetics of the catalyzed reaction have been studied, and a few

*Actually, pure zinc ferrocyanide is not formed, but rather a compound salt with the formula $\text{K}_2\text{Zn}_3[\text{Fe}(\text{CN})_6]_2$.

mechanisms have been proposed (L1, L2). The following mechanism accounts for most of the observed data.



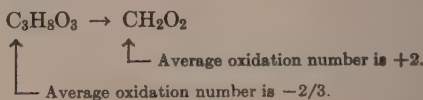
Determination of Organic Compounds with Cerate

(See Sec. 20E.3, p. 470)

Cerate is a strong oxidizing agent that can be heated in aqueous solution for moderate lengths of time without decomposition. This is not true of KMnO_4 or KIO_4 , and standard cerate in HClO_4 is definitely superior to these two reagents in the determination of many organic compounds. The procedure is very simple: an excess of standard cerate is added to the sample in about 4 M HClO_4 , and the mixture is heated for a short time to allow complete reaction. After being cooled to room temperature, the excess cerate is determined by titration with standard FeSO_4 , ferroin being used as an indicator. The oxidation conditions must of course be carefully controlled to keep the reactions stoichiometric.

An excellent short comparison is drawn among various oxidants (KMnO_4 , KIO_4 , and cerate in HClO_4) for organic compounds by Walton (W5), and the behavior of many specific kinds of organic compounds toward these oxidants is described by Smith (S18).

Example. Glycerol ($\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CH}_2\text{OH}$) is oxidized quantitatively to formic acid (HCOOH) by being heated for 15 minutes at 60°C with 50.00 ml of 0.1000 N cerate in 4 M HClO_4 . After reaction, the excess cerate requires 10.6 ml of 0.0500 N Fe(II) for titration to the ferroin end point. What is the weight of glycerol?



There is a change of $2\frac{2}{3}$ electrons per atom of C, or $3 \times 2\frac{2}{3} = 8$ electrons per molecule of glycerol. The equivalent weight of glycerol is $92.096/8$, or 11.512.

The weight of glycerol is therefore

$$[50.00(0.1000) - 10.6(0.0500)] \times 11.512 = 51.5 \text{ mg}$$

meq Ce(IV) reacting with glycerol

*Ce(IV) exists as a chloride complex in chloride medium, so this reaction should be regarded as bimolecular rather than termolecular.

OTHER REDOX METHODS

(See Sec. 20F, p. 470)

Bromate Titrations (K19)

Assayed reagent-grade KBrO_3 has a minimum assay value of 99.8%, and need only be dried at 150°C for a few hours before its use as a primary standard. The solid is stable in air and is nonhygroscopic. Standard KBrO_3 solutions are therefore best made from KBrO_3 as a primary standard, even though they may also be standardized later by titration against primary standard As_2O_3 . KBrO_3 solutions are very stable, and do not require special precautions for storage.

Direct titrations. When titrated directly against sufficiently strong reductants, BrO_3^- is reduced quantitatively to Br^- , and shows 6 eq per mole. As(III) , Sb(III) , Sn(II) , Tl(I) , Fe(CN)_6^{4-} , and many other reductants are titratable in this way. The titration of As(III) with standard KBrO_3 in acid solution is typical. So long as any unoxidized As(III) remains, BrO_3^- is reduced to Br^- .



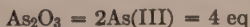
After all As(III) is used up, the first slight excess of BrO_3^- reacts with Br^- to give bromine, which in turn reacts with the indicator to give the end point.



Nonreversible indicators such as methyl orange or methyl red may be used to establish the end point. The chrysoïdins are a more recently discovered class of indicators, which are reversibly decolorized by bromine, and which may lead eventually to wider use of KBrO_3 in direct titrations.

With weaker reducers, BrO_3^- may be reduced only to free bromine, or incompletely to a bromine-bromide mixture. By adding Hg(II) , Br^- is complexed to form undissociated HgBr_2 , which gives a more complete reaction and permits the direct titration to be made. Fe(II) , $\text{H}_2\text{C}_2\text{O}_4$, Mn(II) (oxidized to MnO_2), and nitrite are titratable in this manner.

Example S1. What are the normality and molarity of a KBrO_3 solution, 47.53 ml of which are required to titrate 0.2000 g of As_2O_3 ?



$$\frac{200.0}{197.84/4} \times \frac{1}{47.53} = 0.08508 \text{ N KBrO}_3$$

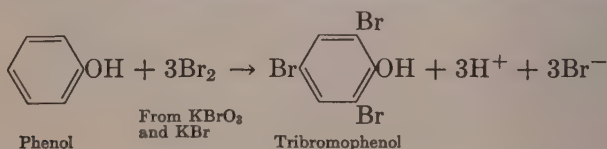
$\text{meq KBrO}_3 \text{ per ml}$
 $\text{meq As}_2\text{O}_3 = \text{meq KBrO}_3 \text{ in 47.53 ml}$

The KBrO_3 molarity is 0.08508/6, or 0.01418 *M*.

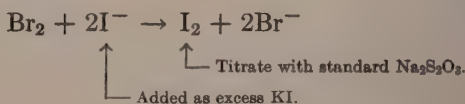
Indirect titrations. KBrO_3 is employed principally as a means of introducing a known amount of free bromine into a system. (Standard bromine solutions cannot be accurately used for this purpose, because of the volatility of bromine.) The system is acidified, excess KBr is added, and then a measured amount of KBrO_3 is added either as solid or as a standard solution. The reaction for the liberation of bromine is



Several indirect determinations are based on this reaction. Some organic compounds such as phenols and anilines may be so determined, since they react quantitatively with free bromine. Thus phenol may be determined by the addition of H_2SO_4 , excess KBr , and a known amount of KBrO_3 , a few minutes being allowed for the bromination.



The excess bromine may be determined in several ways, one of the most popular being the iodimetric.



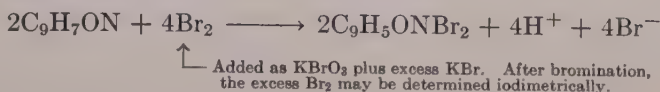
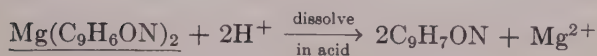
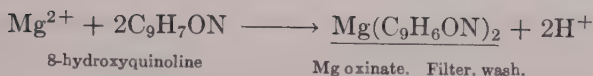
Example S2. To a sample of phenol are added H_2SO_4 , excess KBr , and 50.00 ml of 0.0500 M KBrO_3 . After bromination of the phenol is complete, an excess of KI is added. The resulting mixture requires 8.54 ml of 0.1000 N $\text{Na}_2\text{S}_2\text{O}_3$ for titration. How many grams of phenol are in the sample?

$$\begin{aligned} \left(\begin{array}{c} \text{mmoles phenol} \\ \text{in sample} \end{array} \right) &= \frac{1}{3} \left(\begin{array}{c} \text{mmoles Br}_2 \text{ used} \\ \text{in bromination} \end{array} \right) \\ &= \frac{1}{3} \left[\left(\begin{array}{c} \text{total mmoles} \\ \text{Br}_2 \text{ added} \end{array} \right) - \left(\begin{array}{c} \text{mmoles Br}_2 \text{ titrated} \\ \text{iodimetrically} \end{array} \right) \right] \\ &= \frac{1}{3} \left[(0.0500 \times 50.00 \times 3) - (0.1000 \times 8.54 \times \frac{1}{2}) \right] = 2.358 \end{aligned}$$

mmoles Br_2 formed from KBrO_3
mmoles I_2 , or mmoles excess Br_2
mmoles KBrO_3 added
meq $\text{Na}_2\text{S}_2\text{O}_3$

$$\text{wt. phenol} = 2.358(94.113) = 221.9 \text{ mg}$$

Magnesium, aluminum, and many other metals may be determined indirectly by this method, after precipitation as the oxinates.



In indirect titrations, where reaction between BrO_3^- and Br^- proceeds simultaneously with the oxidation of the sought-for compound, the system contains bromine in intermediate oxidation states, such as free bromine and unipositive bromine. These various oxidation states may react with the reductant at different rates to give different products (especially if the reductant is an organic molecule); then the stoichiometry may depend very critically on the reaction conditions and may not be very reproducible. The selection of conditions to obtain stoichiometrical results for various types of organic compounds has been outlined by Schulek and coworkers (55).

Standard Reducing Solutions (K19)

(See Sec. 20F.2, p. 475)

Ti(III) solutions. Ti(III) is a considerably stronger reducer than Fe(II), and may be used to titrate considerably weaker oxidants.



Twenty per cent TiCl_3 solution is commercially available, and may be used to prepare dilute solutions. Ti(IV) salts are stable in air, and solutions of Ti(IV) salts may be reduced electrolytically, or with amalgamated Zn, to give solutions of Ti(III) salts. Solutions prepared in this way must be standardized after preparation. $\text{K}_2\text{TiF}_6 \cdot \text{H}_2\text{O}$ is a primary standard, and may be fumed with H_2SO_4 to remove fluoride, diluted, and reduced with amalgamated Zn to give a standard Ti(III) solution. Standard Ti(III) solutions must contain excess acid (usually HCl or H_2SO_4) to prevent hydrolysis and precipitation of any Ti(IV) which may be present. Also, the reducing strength of the Ti(III)-Ti(IV) system increases with decreasing acidity, and in weakly acid or alkaline solutions, Ti(III) reacts with water to liberate hydrogen.

Air oxidizes Ti(III) solutions fairly rapidly, and they must be protected from air both in storage and in use. Standard Ti(III) solutions should be stored under an inert atmosphere such as nitrogen. The equipment of Fig. 18.7 (p. 360) may be used without the NaOH tube, and with the air inlet connected to a nitrogen tank. The Bunsen valve

should also open into the inert atmosphere, or at least into a small buffering tube equipped at the other end with a second Bunsen valve. There exist other buret-reservoir arrangements for excluding air, some of which are commercially available.

To carry out a titration under an inert atmosphere, a stream of nitrogen or of CO_2 is passed continually through the titration vessel and allowed to escape into the air. This keeps a blanket of inert gas over the titrated solution. In such titrations, it is advisable to bubble the inert gas through the solution for a short time before beginning the titration, to sweep out any dissolved oxygen.

Primary standard Fe wire is generally used to standardize Ti(III) solutions. The Fe wire is dissolved in acid solution, all Fe is oxidized to Fe(III), and the solution is then titrated with the Ti(III) solution to be standardized, methylene blue or KSCN being used as an indicator. Since the reaction is slow near the end point at 25°C , a temperature of 50°C is used. Standard strong oxidants, such as $\text{K}_2\text{Cr}_2\text{O}_7$ or cerate, may be used to standardize Ti(III) solutions.

The principal use of standard Ti(III) is in the titration of metals without prereduction. Thus Fe(III) may be titrated directly, as described above. Some applications are summarized in Table S20.3.

TABLE S20.3
DETERMINATIONS WITH STANDARD Ti(III)

Substance	Remarks
$\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$	In HCl or H_2SO_4 solution.
$\text{Cu}^{2+} \rightarrow \text{Cu}^+$	In HCl. In H_2SO_4 , Cu metal would be formed.
$\text{Sn}^{4+} \rightarrow \text{Sn}^{2+}$	In HCl.
Strong oxidizers	$\text{Cr}_2\text{O}_7^{2-}$, Ce(IV) , MnO_4^- , ClO_3^- , etc.
Organic compounds	Nitro, nitroso, azo, and hydrazo compounds reduced quantitatively to amines. Also some diketones and quinones. Cr(II) is a better titrant.

Cr(II) solutions. Cr(II) is the strongest standard reducing agent used in redox titrations.



Standard solutions must be stored in the absence of air, and titrations must be performed under inert atmospheres. Standard Cr(II) may be used more advantageously for the same types of titrations as Ti(III); Cr(II) is a stronger reductant, and its reactions are generally faster and more complete.

Cr(II) is a strong enough reductant to liberate hydrogen from dilute

acids, but the rate of this reaction is low. Acid Cr(II) solutions do not decompose appreciably over several days, unless catalytic impurities are present. To avoid such catalysts, very pure materials are used to prepare standard solutions. Chromous solutions should also contain excess acid (HCl or H₂SO₄) to prevent hydrolysis and precipitation of any Cr(III) which might be present.

CrCl₂ or CrSO₄ solutions may be prepared from K₂Cr₂O₇ as a primary standard, by reducing an acid solution of the K₂Cr₂O₇ first to Cr(III) with H₂O₂, boiling to remove excess H₂O₂, and then reducing the Cr(III) to Cr(II) with amalgamated Zn. Chromous solutions may also be standardized after preparation. Iron wire, Cu metal, or K₂Cr₂O₇ may be used as primary standards, according to methods outlined in Table S20.4.

End points in titrations with standard Cr(II) are established potentiometrically. A platinum electrode suffices to establish the *E* of the titrated solution against a standard electrode, provided that the *E* of the titrated solution does not become low enough during titration to permit liberation of hydrogen, since this reaction is catalyzed on the Pt surface.

Titrations performable with standard Cr(II) are summarized in Table S20.4.

TABLE S20.4
TITRATIONS WITH STANDARD Cr(II)

Substance	Remarks
Fe ³⁺ → Fe ²⁺	In HCl or H ₂ SO ₄ solution.
TiO ²⁺ → Ti ³⁺	In hot HCl solution.
Cu ²⁺ → Cu ⁺	In HCl solution. CuCl ₄ ⁼ is slowly reduced to Cu metal in excess Cr(II) after the equivalence point is passed.
Cu ²⁺ → Cu.....	In chloride-free solutions.
Mo(VI) → Mo(V) → Mo(III)...	In hot HCl solution. Double end point.
V(V) → V(IV) → V(III).....	In 10% H ₂ SO ₄ . Double end point.
H ₃ AsO ₄ → H ₃ AsO ₃	
Bi ³⁺ → Bi.....	In HCl or H ₂ SO ₄ solution.
Ag ⁺ → Ag.....	Hot, chloride-free solution.
Cr ₂ O ₇ ⁼ → Cr ³⁺	Rate of reaction low. Hence add excess FeSO ₄ to the dichromate. Titrate the Fe(III) formed with standard Cr(II).
Strong oxidizers.....	Ce(IV), MnO ₄ ⁼ , ClO ₃ ⁼ , etc.
Sn ⁴⁺ → Sn ²⁺	Hot HCl solution.
O ₂ → H ₂ O.....	CrCl ₂ solution is a very effective absorbent for oxygen in gas samples.
Hg ²⁺ → Hg _(l)	
Au(III) → Au.....	
Organic compounds.....	Same ones as in Table S20.3, but action of Cr(II) is faster and cleaner than with Ti(III) (J4).

PREPARATION OF STUDENT ORE SAMPLES

(See Exps. 20.1–20.3, pp. 476–93)

Ore samples may vary considerably in extractability, and in the interfering substances that they contain. In order that all samples may be of similar extractability, it is recommended that two large master lots of finely ground ore (200 mesh or finer) be used to prepare all unknown samples in a series. Suppliers of such ores are listed in manufacturer's catalogs. The two master lots should be of similar origin, but should differ in content of the sought-for element.

Thus to prepare an unknown Fe ore series ranging from 50 to 60% Fe_2O_3 , one master lot should contain about 50% Fe_2O_3 and the other about 60% Fe_2O_3 . The individual members of the series may be prepared by mixing quantitatively weighed portions of the two master lots by a procedure similar to that described on page 694. Before the portions are weighed out, the master lots should be dried overnight at 150–160°C. Only the Fe contents of the two master lots need be determined by analysis, and the compositions of the mixtures prepared therefrom may be calculated. It is necessary to tumble such mixtures before student samples are withdrawn.

An appropriate limestone series ranges from 35 to 45% CaO . The two master lots should be dried overnight at 100–110°C before the portions for the individual members of the series are weighed out.

For student work, a suitable series of Cu ore samples ranges from 17 to 20% Cu. Most Cu ores have a rather low Cu content, but hand-picked master samples of sufficiently high Cu content are available. The two master samples should be dried overnight at 130–150°C before being weighed out for the individual samples.

SUPPLEMENTARY QUESTIONS*Section 20A*

S1. Summarize the various methods of eliminating or inactivating the excess of preoxidant or prereductant before the titration of the sought-for substance, giving a specific example for each method.

S2. For any one element, starting with an air-stable oxidation state, write balanced equations to show its oxidation or reduction by each of three of the preoxidants or prereductants listed in Table S20.1 (p. 822).

S3. On the basis of information given in Table S20.1, devise volumetric methods for determining each member of the following pairs of elements in mixtures containing approximately equivalent amounts of the two. (a) Fe and Ti; (b) Fe and Mo; (c) Fe and Cr; (d) Cr and U; (e) Ti and Cr; (f) Ti and V.

S4. Describe how to determine V in the presence of Fe and Cr, using liquid amalgams.

S5. Write the equation for the formation of H_2O_2 when air is introduced to the Zn reductor.

S6. List those elements that would be reduced to metals by the Zn reductor.

S7. With the aid of the TSP, fill in some of the blank spaces in Table S20.1. What limitation must be placed on the added figures?

Section 20B

S1. If $[\text{H}^+]$ in the titrated solution is 1.0 *M*, which is the positively charged electrode in the electrochemical cell on page 829? Write the reactions that occur at each electrode when current is permitted to flow.

S2. Cyanide forms the complex ion $\text{Ag}(\text{CN})_2^-$, as well as the insoluble salt AgCN . Sketch a rough curve for the titration of a KCN solution with standard AgNO_3 (W5).

Section 20C

S1. A main source of error in the Volhard determination of Mn is the coprecipitation of Mn^{2+} by MnO_2 . Give the sign of the error.

S2. Write balanced equations for the determination of Hg_2^{2+} , TeO_3^- , or SeO_3^- by titration with standard KMnO_4 in pyrophosphate medium.

S3. Show that the sum of Eqs. Sc–Sg (p. 839) gives the stoichiometrical equation Sa.

S4. Consider the composition and charge of the reacting species, and explain why Cl^- might be expected to react less rapidly with Mn(VII) than with lower oxidation states of Mn, such as Mn(IV) and Mn(III) (p. 842).

S5. Speculate as to why the induced oxidation of Cl^- does not occur when Fe(II) is titrated with Ce(IV), which is just as strong an oxidant as MnO_4^- .

S6. Speculate as to why the induced oxidation of Cl^- does not occur when Fe(II) is titrated with $\text{K}_2\text{Cr}_2\text{O}_7$, when Cr shows intermediate oxidation states comparable to Mn.

Section 20D

S1. Write balanced chemical equations outlining a determination from Table S20.2A (p. 844). Repeat for Table S20.2B.

S2. Why is starch inappropriate for the ICl end point?

S3. Explain why the redox normality of a standard iodine solution cannot be determined by titration against standard KIO_3 .

S4. An attempt is made to standardize an $\text{Na}_2\text{S}_2\text{O}_3$ solution containing Na_2CO_3 as a preservative by means of the iodate-iodide reaction, using standard HCl as a titrant. Explain the direction of the error.

S5. Describe the error due to absorption of CO_2 from the air, when the iodate-iodide reaction is used to standardize an acid solution (B23).

S6. Write balanced equations for the cleavage of the following compounds by periodate: diacetyl ($\text{CH}_3\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_3$); pyruvic aldehyde ($\text{CH}_3\cdot\text{CO}\cdot\text{CHO}$); glyoxal ($\text{CHO}\cdot\text{CHO}$); ethanolamine ($\text{CH}_2\text{OH}\cdot\text{CH}_2\text{NH}_2$); glycolic aldehyde ($\text{CH}_2\text{OH}\cdot\text{CHO}$); serine ($\text{CH}_2\text{OH}\cdot\text{CHNH}_2\cdot\text{COOH}$); threonine ($\text{CH}_3\cdot\text{CHOH}\cdot\text{CHNH}_2\cdot\text{COOH}$).

S7. Speculate as to how Cu^{2+} might catalyze the air-oxidation of $\text{Na}_2\text{S}_2\text{O}_3$. Repeat for VO^{2+} .

S8. A gas stream contains about 80% N_2 , 20% O_2 , and 0.1% O_3 . Describe how the O_2 and O_3 may be determined.

S9. As(III) may be titrated with standard iodine in the presence of Cu(II), provided that the solution is neutral and contains an excess of NaK tartrate, which forms a Cu(II)-tartrate complex. After the As(III) end point is reached, H_2SO_4 is added to increase the acidity; then excess KI is added and the solution is titrated with standard $\text{Na}_2\text{S}_2\text{O}_3$ to give the Cu content. Explain the chemistry of this method of analysis, using chemical equations (K18).

S10. Describe the appearance of the titrated solution at various points in the titration of 0.10 *M* KI with 0.10 *M* Ce(IV), taking into account the precipitation of iodine after the titration is under way (L12).

S11. Outline a procedure whereby a worker may standardize a $\text{K}_2\text{Cr}_2\text{O}_7$ solution against a standard base that he has on hand.

Section 20E

S1. Based on the observation that the rate of the Ce(IV)-As(III) reaction is directly proportional to $[\text{I}^-]$, outline a procedure for the determination of low concentrations of I^- , and check in the literature (D9).

S2. Postulate a mechanism for the catalysis of the Ce(IV)-As(III) reaction by Mn(II).

S3. Write the balanced equation for the oxidation of pyruvic acid ($\text{CH}_3\cdot\text{CO}\cdot\text{COOH}$) to acetic acid and CO_2 by Ce(IV). How many equivalents are there per mole of pyruvic acid?

Section 20F

S1. Postulate a mechanism to show the catalytic action of Ag in the oxidation of Cr(III) to Cr(VI) by persulfate. It has been shown that Ag(II) exists in strongly oxidizing media.

S2. Write an equation for the direct titration with standard KBrO_3 of one of the substances mentioned on page 853.

S3. Write the structural formula of 8-hydroxyquinoline and its bromination product.

S4. Write balanced equations showing (a) the titration of FeCl_3 with standard TiCl_3 , using KSCN as an indicator; (b) the determination of one of the substances in Table S20.3 (p. 856).

S5. Using the TSP, show that TiCl_3 can reduce CuSO_4 to metallic Cu. In HCl solutions, why is Cu(I) formed instead of the metal?

S6. Compare the advantages and disadvantages of standard CrCl_2 with standard $\text{K}_2\text{Cr}_2\text{O}_7$ in determining Fe (a) in pure aqueous solutions containing about 0.1 *M* FeCl_3 ; (b) in ores.

S7. Write balanced equations for (a) one of the titrations of Table S20.4 (p. 857); (b) the preparation of CrSO_4 from $\text{K}_2\text{Cr}_2\text{O}_7$ as a primary standard; (c) the reduction of HCl by CrCl_2 ; (d) the titration of dichromate with Cr(II).

S8. Write balanced half-reactions for reduction of the following compounds, and give the number of equivalents per mole of each compound when titrated with Cr(II), as in Table S20.4. (a) *p*-nitrosophenol ($\text{NO}\cdot\text{C}_6\text{H}_4\cdot\text{OH}$), reduced to *p*-aminophenol ($\text{NH}_2\cdot\text{C}_6\text{H}_4\cdot\text{OH}$); (b) nitrobenzene ($\text{C}_6\text{H}_5\cdot\text{NO}_2$), reduced to aniline ($\text{C}_6\text{H}_5\cdot\text{NH}_2$); (c) azobenzene ($\text{C}_6\text{H}_5\cdot\text{N}=\text{N}\cdot\text{C}_6\text{H}_5$), reduced to aniline ($\text{C}_6\text{H}_5\cdot\text{NH}_2$).

S9. Draw a modification of the apparatus of Fig. 18.7 (p. 360), for storage and withdrawal of TiCl_3 solutions. Consider an arrangement whereby nitrogen would not be used extravagantly. Compare your apparatus with other types described in the literature.

SUPPLEMENTARY PROBLEMS

Section 20A

S1. A 25.00-ml aliquot of a solution containing Fe and U in unknown oxidation states is reduced with Zn amalgam, after which 35.20 ml of 0.1000 *N* KMnO_4 are required for titration. After another 25.00-ml aliquot is passed through an Ag reductor, 29.65 ml of the KMnO_4 are required for titration. Calculate the Fe and U contents of the original solution, in terms of (a) moles per liter; (b) grams of Fe_2O_3 per liter and grams of U_3O_8 per liter. Assume that Zn reduces U quantitatively to U(III).
Ans. (a) 0.07420 *M* Fe, 0.02220 *M* U.

S2. A sample containing Fe(III) and V(V) is made up to 250 ml. A 25.00-ml aliquot is passed through a zinc reductor, and then is titrated with 0.1000 *N* dichromate, 44.62 ml being required. Another 25.00-ml portion is titrated after passage through a silver reductor, 23.45 ml of 0.1000 *N* Ce(IV) being required. Calculate the weight in grams of both the iron and the vanadium in the sample.

S3. A 25.00-ml aliquot of a solution containing Ti and V is reduced with Zn amalgam, after which the mixture requires 38.25 ml of 0.1000 *N* KMnO_4 for titration. Another 50.00-ml aliquot of the same solution, after being passed through an Ag reductor, requires 6.25 ml of 0.1000 *N* KMnO_4 for titration. Calculate the grams per liter of Ti and of V in the original solution. *Ans.* 0.637 g V/l, 5.532 g Ti/l.

S4. If V_s and V_a are the volumes of *n N* KMnO_4 required after reduction with Zn and Ag, respectively, express the answers to Prob. S3 in terms of V_s , V_a , and *n*.

Section 20B

S1. Consider how activity effects alter the titration curve of Fig. 20.1 (p. 442). Show that while the equivalence-point *E* may be appreciably altered, the equivalence-point volume is not.

S2. A titration is performed under the conditions of Fig. 20.1, except that the original solution contains 0.0500 *M* $\text{Fe}_2(\text{SO}_4)_3$ as well as 0.1000 *M* FeSO_4 . Calculate *E* initially and at the equivalence point. Compare the titration curve with that of Fig. 20.1.

S3. Calculate the equivalence-point *E* for the Fe(II)-dichromate titration of Ex. S2, page 826, for the three following sets of conditions, and compare results. (a) *C* = 0.100 *N*, $[\text{H}^+] = 1.00 \text{ M}$; (b) *C* = 0.0100 *N*, $[\text{H}^+] = 1.00 \text{ M}$; (c) *C* = 0.100 *N*, $[\text{H}^+] = 0.100 \text{ M}$.
Ans. (a) 1.26 v; (b) 1.27 v; (c) 1.14 v.

S4. Show that the *E* of the Ag-AgCl electrode is linearly dependent upon *pAg* of the solution in which the electrode is immersed.

S5. Suppose that 0.100 *M* HCl is titrated with 0.100 *M* NaOH. What would be the change in *E* of an Ag-AgCl electrode from the beginning of the titration to the equivalence point? What would be the change in *E* of a glass electrode? Could the Ag-AgCl electrode be used as a reference electrode?

Ans. 18 mv; 355 mv; yes.

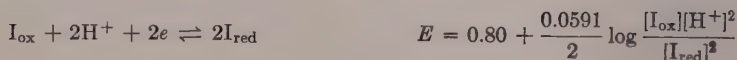
S6. In Prob. S5, calculate the change in *E* for each electrode in passing from 1% before the equivalence point to the equivalence point.

S7. The behavior of an indicator is described by

$$\text{I}_{\text{ox}} + 2\text{H}^+ + 2e \rightleftharpoons \text{I}_{\text{red}} \quad E = 0.52 + \frac{0.0591}{2} \log \frac{[\text{I}_{\text{ox}}][\text{H}^+]^2}{[\text{I}_{\text{red}}]}$$

(a) Give the transition potentials of this indicator when $[\text{H}^+]$ is 1.0 *M*, and also when $[\text{H}^+]$ is 0.010 *M*. (b) Estimate the magnitude of the transition range in a solution of a given $[\text{H}^+]$.
Ans. (a) 0.52, 0.40 v; (b) 0.0591 v.

S8. The behavior of an indicator is described by



(a) Give the transition potentials for total indicator concentrations of 0.0010 and 0.00010 *M*, if $[\text{H}^+]$ is 1.0 *M* in each case. (b) Estimate the magnitudes of the transition ranges for total indicator concentrations of 0.0010 and 0.00010 *M*, if $[\text{H}^+]$ is 1.0 *M* in each case. Compare answers with those of Prob. S7.

S9. An indicator must be chosen for the titration of A_{ox} with B_{red} .



In terms of E_{A}° and E_{B}° , state within what range the transition range of an indicator may fall, in order that it may transit completely within the range from 0.01% before the equivalence point to 0.01% after.

Ans. From $E_{\text{A}}^\circ - 0.236 \text{ v}$ to $E_{\text{B}}^\circ + 0.236 \text{ v}$.

S10. Write the half-reaction for the reduction in aqueous solution of insoluble Sb_2O_3 to metallic Sb. Show how an Sb electrode coated with Sb_2O_3 may function as a pH electrode (I2).

S11. The titration of 50.00 ml of 0.1000 *M* ZnCl_2 with standard 0.05000 *M* $\text{K}_4\text{Fe}(\text{CN})_6$ may be followed potentiometrically by adding some $\text{K}_3\text{Fe}(\text{CN})_6$ to the original solution (say 0.00200 *M*), and following the change in *E* due to the change in $[\text{Fe}(\text{CN})_6^-]/[\text{Fe}(\text{CN})_6^{4-}]$ as the titration proceeds. (Zinc ferrocyanide is insoluble, but zinc ferricyanide is soluble.)

(a) Sketch apparatus for making the potential measurements.

(b) Calculate *E* in the region of the equivalence point, when 49.90, 50.00, and 50.10 ml of the $\text{K}_4\text{Fe}(\text{CN})_6$ have been added. (Assume that $\text{Zn}_2\text{Fe}(\text{CN})_6$ is formed, with a solubility product as given in Appendix V.) *Ans.* (b) 0.50 v (for 50.00 ml).

S12. Draw a rough curve for the titration of 50.00 ml of one of the following solutions with standard 0.1000 *M* KMnO_4 , and estimate the equivalence-point *E*'s. Assume that $[\text{H}^+]$ is 1.00 *M* at each equivalence point. (a) 0.1000 *M* VCl_2 ; (b) 0.1000 *M* MoCl_3 ; (c) 0.1000 *M* UCl_3 .

S13. Draw a rough curve for the titration of 50.00 ml of 0.1000 *M* H_2MoO_4 with standard 0.1000 *M* CrCl_2 , and estimate the equivalence-point *E*'s. Assume that $[\text{H}^+]$ is 1.00 *M* at each equivalence point. *Ans.* 0.00 v; -0.13 v.

S14. A 50.00-ml portion of a solution containing 0.01000 *M* $\text{K}_2\text{Cr}_2\text{O}_7$ and 0.05000 *M* CuSO_4 is titrated with 0.1000 *M* $\text{Ti}_2(\text{SO}_4)_3$. Estimate the equivalence-point *E*'s, if $[\text{H}^+]$ is 1.00 *M* at each equivalence point. Select or devise visual indicators for the two end points (R1).

S15. A solution containing 0.1000 *M* $\text{V}_2(\text{SO}_4)_3$ and 0.1000 *M* FeSO_4 is titrated with standard 0.1000 *M* KMnO_4 , and with $[\text{H}^+] = 1.00 \text{ M}$ throughout the titration. Show that the titration curve has no significant inflections at any of the three equivalence points.

Section 20C

S1. Give the equivalents per mole of formaldehyde and of formate, when determined with KMnO_4 in basic solution. *Ans.* 4, 2.

S2. The titer of a KMnO_4 solution is 8.00 mg of sodium formate per ml, when used in basic solution. What is the Fe titer of the KMnO_4 , when used in acid solution?

S3. A 20.00-ml sample of an aqueous solution containing formic acid (HCOOH) and H_2SO_4 requires 45.05 ml of 0.1000 *N* base for neutralization to the phenolphtha-

lein end point. After making the solution basic, 30.72 ml of standard KMnO_4 are required to titrate the formic acid. (The KMnO_4 is 0.200 *N*, with respect to reduction to MnO_2 .) What is the composition of the original sample?

Ans. 0.0870 *M* H_2SO_4 , 0.0512 *M* formic acid.

S4. When determined with alkaline permanganate, methanol (CH_3OH) is oxidized to carbonate. Write the balanced chemical equation. Devise an example to illustrate calculation of the amount of methanol in a sample from the equivalents of permanganate consumed.

S5. In the Volhard method for Mn, what is the normality of a 0.100 *M* KMnO_4 solution? What is the equivalent weight of Mn_2O_3 in a sample, all Mn being pre-reduced to Mn(II) before titration? Repeat the answers for the Lingane-Karplus method.

Ans. 0.300 *N*, 38.1353 (for Volhard method).

S6. After prereduction, the Mn in a 0.2000-g ore sample requires 45.90 ml of 0.1000 *M* KMnO_4 for titration by the Volhard method. What is the % MnO_2 in the ore?

S7. What weight of Fe ore should be taken for analysis so that twice the number of milliliters of 0.1000 *N* KMnO_4 required for titration will give the Fe content as % FeCO_3 ?

Ans. 0.5793 g.

S8. What must be the normality of a KMnO_4 solution, so that each milliliter used in a titration of Fe(II) represents one per cent of FeO, when a 0.600-g sample is taken?

S9. A 0.8000-g sample contains only CaC_2O_4 and PbC_2O_4 , and requires 70.00 ml of 0.1260 *N* KMnO_4 for titration. What is the composition of the mixture?

Ans. 0.4153 g PbC_2O_4 , 0.3847 g CaC_2O_4 .

S10. A 0.1750-g sample containing only NaNO_2 and RbNO_2 requires 46.85 ml of 0.1000 *N* KMnO_4 for titration. Calculate the composition.

Section 20D

S1. Excesses of KI and KIO_3 are added to a 1.000-g sample containing only K_2SO_4 and KHSO_4 . The iodine liberated requires 38.26 ml of 0.1500 *N* $\text{Na}_2\text{S}_2\text{O}_3$ for titration. Give the % KHSO_4 in the sample. Why could this method not be used to analyze a mixture of Na_2CO_3 and NaHCO_3 ?

Ans. 78.2%.

S2. A 5.325-g sample containing only NaCl and $\text{Na}_2\text{S}_2\text{O}_3$ is dissolved in water and made up to 250 ml in a volumetric flask. To an acidified solution containing excess ICl, 50.00 ml of the sample solution are added. If 27.26 ml of 0.1000 *N* KIO_3 are required for titration to the ICl end point, what is the % $\text{Na}_2\text{S}_2\text{O}_3$ in the original sample?

S3. To 25.00 ml of a solution containing KClO_3 as the only solute, 50.00 ml of 0.1000 *M* KI and an excess of acid are added. After reaction, the excess KI remaining and the iodine formed require 30.36 ml of 0.0500 *M* KIO_3 for titration to the ICl end point. What is the molarity of the original KClO_3 solution?

Ans. 0.0262 *M*.

S4. A 0.2325-g sample of As_2O_3 is dissolved in cold conc. HCl and transferred to a glass-stoppered flask containing 5 ml of CCl_4 . This solution is titrated with a KIO_3 solution until the iodine color first formed just disappears. If 48.96 ml of the KIO_3 are required, calculate the KIO_3 concentration. Write balanced equations for the reactions that occur.

S5. Using equations, outline a procedure whereby a steel containing about 1% Mn may be analyzed for Mn as permanganate, KIO_4 being used as a preoxidant. Include a sample calculation.

S6. A 0.800-g aqueous sample of ethylene glycol ($\text{CH}_2\text{OH}\cdot\text{CH}_2\text{OH}$, permanent antifreeze) is treated with 100.0 ml of 0.1000 *M* KIO_4 , and time allowed for cleavage. After reaction, 50.00 ml of 0.1000 *M* Na_3AsO_3 are added, after which 29.56 ml of

0.1000 *N* iodine are required for titration. Calculate the percentage of ethylene glycol in the original sample.

S7. The amino acid, serine ($\text{CH}_2\text{OH}\cdot\text{CHNH}_2\cdot\text{COOH}$), may be determined by measuring the formaldehyde resulting from Malaprade cleavage. Most of the other naturally occurring amino acids do not have the terminal groupings required to give formaldehyde, and do not interfere. What is the percentage of serine in a 2.00-g sample which yields 10.2 mg of formaldehyde? Calculate the millimoles of NH_3 liberated. What is the other cleavage product?

Ans. 1.78%, 0.340, glyoxylic acid.

S8. What weight of Cu ore should be taken for analysis in order that each milliliter of 0.0800 *N* $\text{Na}_2\text{S}_2\text{O}_3$ required for titration will represent 2.000% CuS in the ore?

S9. Sulfur in steel may be determined by burning the sample in a stream of oxygen and absorbing the SO_2 produced in a solution of NaOH. The basic solution is neutralized and the SO_2 determined by titration with standard iodine. What weight of sample must be taken in order that each milliliter of 0.01000 *N* iodine will represent 0.01000% S in the sample?

Ans. 1.603 g.

S10. A mixture containing only $\text{K}_2\text{Cr}_2\text{O}_7$ and KMnO_4 weighs 1.800 g. After it is treated with excess KI in acid solution, 45.23 ml of 0.1000 *N* $\text{Na}_2\text{S}_2\text{O}_3$ are required for titration. Calculate the % Mn and % Cr in the mixture.

S11. A 0.2000-g alloy sample contains only As and Sb. After dissolution and conversion to the trivalent states, 42.14 ml of 0.1000 *N* iodine are required for titration. Calculate the composition of the sample.

Ans. 45.0% As, 55.0% Sb.

S12. Draw a rough curve for the titration of 50.00 ml of 0.1000 *M* KI with 0.1000 *M* KMnO_4 to the ICl end point. Estimate equivalence-point E 's. Assume that $[\text{H}^+]$ and $[\text{Cl}^-]$ are each 1.00 *M* at each equivalence point. Speculate as to whether or not an inflection would be observed at the iodate equivalence point. (E° is 1.06 v for the half-reaction, $2\text{ICl}_2^- + 2e \rightleftharpoons \text{I}_2 + 4\text{Cl}^-$.)

S13. H_3AsO_4 may be determined indirectly as follows: Add an excess of KI to the acidified solution, liberating iodine. Titrate the iodine with standard $\text{Na}_2\text{S}_2\text{O}_3$, using starch indicator.



(a) Calculate the equilibrium constant for reaction 1. (b) If a solution containing 0.0100 *M* H_3AsO_4 is made 0.0500 *M* in KI, what would $[\text{H}^+]$ have to be in order that 99.9% of the H_3AsO_4 will be reduced? Assume that all iodine exists as I_3^- . (c) If the iodine produced in reaction 1 is removed by titration with $\text{Na}_2\text{S}_2\text{O}_3$, reaction 1 proceeds further toward completion. Assuming that $[\text{I}_3^-]$ must be 1.0×10^{-6} *M* for detection of the end point, what would $[\text{H}^+]$ have to be for 99.9% of the H_3AsO_4 to be reduced at the end point?

Ans. (a) 6.0; (b) 460 *M*.

Section 20E

S1. What should be the normality of a cerate solution, if each milliliter is to represent one per cent of Fe_2O_3 in a sample? Assume that a 1.000-g sample is used.

Ans. 0.1253 *N*.

S2. What sample weight should be taken if each milliliter of 0.1000 *N* cerate is to represent one per cent of TiO_2 in the sample?

S3. What is the number of equivalents per mole for each of the following compounds which can be oxidized quantitatively by cerate to the products shown:

(a) formaldehyde (HCHO) to formic acid (HCOOH); (b) glucose ($\text{CH}_2\text{OH}\cdot(\text{CHOH})_4\cdot$

CHO) to formic acid; (c) benzoic acid ($\text{C}_6\text{H}_5\cdot\text{COOH}$) to CO_2 ; (d) biacetyl ($\text{H}_3\text{C}\cdot\text{CO}\cdot\text{CO}\cdot\text{CH}_3$) to acetic acid; (e) malonic acid ($\text{HOOC}\cdot\text{CH}_2\cdot\text{COOH}$) to CO_2 .

Ans. (b) 12.

S4. How many milliliters of 1.000 *N* cerate in HClO_4 are required to oxidize 1.000 g of formaldehyde (CH_2O) to formic acid (HCOOH)?

S5. A 25.00-ml portion of an aqueous solution of glyoxal ($\text{CHO}\cdot\text{CHO}$) is oxidized to formic acid by being heated after the addition of 50.00 ml of 0.1500 *N* cerate in HClO_4 . After reaction occurs, the remaining cerate takes 7.30 ml of 0.1000 *N* Fe(II) for titration to the ferroin end point. What is the molarity of the glyoxal solution?

Ans. 0.1354 *M*.

S6. With proper control of conditions, the oxidation of glycerol ($\text{CH}_2\text{OH}\cdot\text{CHOH}\cdot\text{CH}_2\text{OH}$) and of ethylene glycol ($\text{CH}_2\text{OH}\cdot\text{CH}_2\text{OH}$) with Ce(IV) may be carried quantitatively either to formic acid (HCOOH) or to CO_2 . Give the equivalents per mole for each compound for each of the two kinds of oxidation. Outline how such data could be used in the analysis of a mixture of the two compounds, and work out an illustrative example. Discuss the accuracy of the procedure.

Section 20F

S1. Give the titer of a 0.1000 *M* KBrO_3 solution in milligrams per milliliter for each of the following substances. (a) As_2O_3 ; (b) TiCl_3 ; (c) $\text{K}_4\text{Fe(CN)}_6$; (d) FeSO_4 ; (e) MnCl_2 ; (f) KNO_2 ; (g) phenol, $\text{C}_6\text{H}_5\text{OH}$; (h) MgCl_2 .

Ans. (b) 71.9 mg/ml.

S2. How many milliliters of 0.1432 *N* KBrO_3 would 0.1596 g of pure KNO_2 require for titration?

S3. A 0.2770-g sample of stibnite (Sb_2S_3) is dissolved under such conditions that all Sb is converted to SbCl_3 , and all S is oxidized to H_2SO_4 . Titration of the SbCl_3 requires 29.89 ml of 0.1065 *N* KBrO_3 . Calculate the Sb content as % Sb_2S_3 .

Ans. 97.6%.

S4. What is the equivalent weight of Al when it is determined as outlined on page 855?

S5. The Mg in a sample containing MgCl_2 and NaCl is precipitated as the oxinate. After being filtered and washed, the Mg oxinate is dissolved in excess acid. Excess KBr and 25.00 ml of 0.05000 *M* KBrO_3 are added to the oxinate solution. After bromination is complete, excess KI is added. Titration of the liberated iodine requires 3.02 ml of 0.1000 *N* $\text{Na}_2\text{S}_2\text{O}_3$. What is the weight of MgCl_2 in the sample?

Ans. 85.68 mg.

S6. *X* ml of 0.1000 *M* KBrO_3 are added to *S* g of a sample containing phenol ($\text{C}_6\text{H}_5\text{OH}$) together with excess acid and KBr . After bromination is complete, excess KI is added, and the resulting mixture requires *Y* ml of 0.1000 *N* $\text{Na}_2\text{S}_2\text{O}_3$ for titration. Express the % phenol in the sample.

S7. What must be the normality of a KBrO_3 solution if each milliliter required in titration is to represent 20.00 mg of As_2O_3 in the sample?

Ans. 0.4044 *N*.

S8. The oxygen content of a gas stream is determined by 3.00 l of the gas being bubbled through a solution containing 50.00 ml of 0.1000 *N* CrSO_4 . After absorption is complete, titration of the excess Cr(II) requires 8.56 ml of 0.0830 *N* KMnO_4 . Calculate the milligrams of oxygen per liter of the gas stream.

S9. A 25.00-ml portion of an aqueous solution contains only $(\text{NH}_4)_2\text{MoO}_4$ and MoO_2Cl . For titration to a first end point, 9.26 ml of 0.1000 *N* CrCl_2 are required. For titration from the first to the second end point, 47.31 ml more of the CrCl_2 are required. Calculate the composition of the original solution.

Ans. 0.03704 *M* $(\text{NH}_4)_2\text{MoO}_4$, 0.05758 *M* MoO_2Cl .

S10. A 25.00-ml portion of an aqueous solution containing only $(\text{NH}_4)_2\text{MoO}_4$ is acidified and titrated with standard 0.1000 N CrSO_4 . (a) If 18.51 ml of the CrSO_4 are required to the first end point, what is the molar concentration of the $(\text{NH}_4)_2\text{MoO}_4$ solution? (b) How much CrSO_4 solution would be required from the first to the second end points? (c) Write balanced equations for the titration steps. The solute species for Mo(VI), Mo(V), and Mo(III) are MoO_4^- , MoO_2^+ , and Mo^{3+} , respectively.

S11. Calculate the equilibrium composition of a solution that originally contains 0.0200 M TiOCl_2 , 0.0200 M CrCl_2 , and 0.0500 M HCl .

Ans. 0.0200 M CrCl_3 , 0.0200 M TiCl_3 ,
0.0100 M HCl , 9.7×10^{-5} M CrCl_2 , 9.7×10^{-5} M TiOCl_2 .

S12. Draw a rough curve for the titration with 0.1000 M TiCl_3 of 50.00 ml of a solution containing 0.1000 M SnCl_4 and 0.1000 M FeCl_3 . Estimate equivalence-point E' s.

SPECTROPHOTOMETRY

COMPONENTS OF THE SPECTROPHOTOMETER

(See Sec. 21B.1, p. 510)

This section consists of an elementary description of the component parts that are fundamental to all spectrophotometers. More detailed information is given in treatises, together with instrument design and descriptions of commercially available instruments (M14, W16).

For a source, most instruments have an ordinary incandescent light bulb, such as an automobile headlight. It is a characteristic of incandescent sources that the energy distribution over the spectrum is not uniform. That is, the intensity of the light emitted varies with wavelength, as shown in Fig. S21.1. The energy distribution depends upon the operating temperature of the filament, which in turn depends very

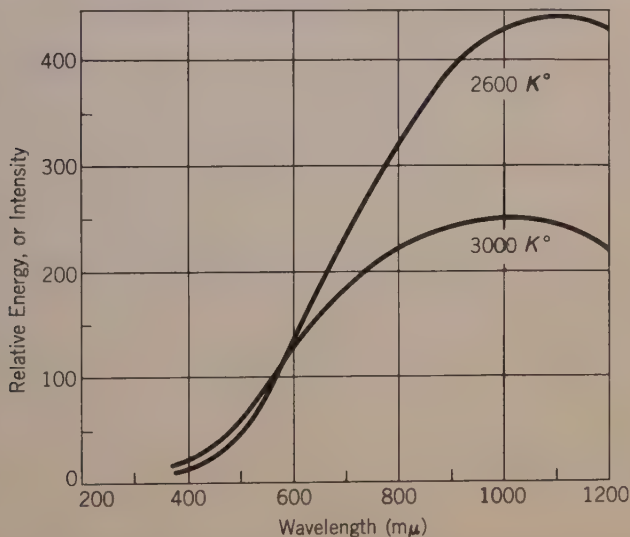


FIG. S21.1. Spectral Energy Distribution of an Incandescent Source (Reprinted from M. G. Mellon, *Analytical Absorption Spectroscopy* [New York: Wiley, 1950], Fig. 5.9, by permission of the publisher.)

critically upon the electric power supplied to the filament. Since the intensity of the source must be kept constant for high precision, many instruments have voltage-controlling devices to ensure a constant power supply to the filament. (This is especially important for instruments deriving power from an ordinary alternating 110-v line, which may show fluctuations of 10–20 v.)

The light-dispersing element may be either a grating or a prism. Gratings are of two types, transmission and reflection. Compared with prisms, gratings have the advantages of lower expense and uniform dispersion throughout the spectrum. Also, since the light is reflected, there is no absorption within a reflection grating. On the other hand, gratings suffer from an impure spectrum—that is, the emergent light at any point in the spectrum is contaminated by light of other wavelengths than that for which the slit is set. However, this disadvantage may be partially overcome by proper design and the use of filters. A prism must be transparent in the wavelength region of interest. Glass prisms are satisfactory for the visible range, but absorb in the ultraviolet and infrared regions. Quartz prisms are useful in the ultraviolet down to $220\text{ m}\mu$; rock-salt prisms may be used in the infrared from 8 to $15\text{ }\mu$. The principal advantage of the prism over the grating is the greater purity of its spectrum.

The slit in some inexpensive grating instruments may be a simple, fixed affair. In more elaborate instruments the slit width may be adjusted to vary the wavelength interval.

The absorption cells in some inexpensive instruments are simply high-quality test tubes, matched and tested to be of certain dimensions. For other instruments, rectangular cells with plane, parallel, flat, polished faces are used.

The photocell may be of two types. The simplest is the photovoltaic (or barrier-layer) cell, across which the light develops an electric potential. If the resistance in the measuring circuit is kept small, the light generates a current that is sufficiently large to be measured with an inexpensive microammeter, and that is proportional to the intensity of the light beam. A second type of photocell is the photoemissive type. When a potential is applied, light striking the cathode liberates electrons, which flow to the anode, generating an electric current. This current is very small and must be amplified before it may be measured with inexpensive meters; therefore such photocells have associated amplifying systems. Photoemissive cells are much more sensitive to light than the photovoltaic type, and therefore permit narrower regions of the spectrum to be isolated.

The response of a photocell to equal intensities of light of different

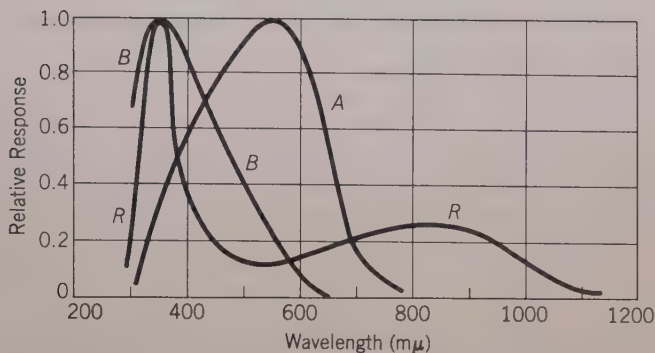


FIG. S21.2. Relative Response of Typical Photocells—Curve A: A barrier-layer cell. Curve R: A "red-sensitive" photoemissive tube. Curve B: A "blue-sensitive" photoemissive tube. (Reprinted from M. G. Mellon, *Analytical Absorption Spectroscopy* [New York: Wiley, 1950], Fig. 5.11, by permission of the publisher.)

wavelengths is not the same, but varies with wavelength. Response curves for typical photocells are given in Fig. S21.2.

Spectrophotometer components may be assembled in a variety of ways to give a variety of instruments.

Single beam instruments are ones that accommodate only one specimen at a time. An absorbance measurement is made on the sample, which is then removed to permit an absorbance measurement on the standard.

On the other hand, there are *double beam instruments* that permit simultaneous comparison of the sample and standard, and that read out the ratio (or log ratio) of the transmittances. Such instruments are inherently more precise and elaborate than the single beam instruments.

Recording spectrophotometers are also available that automatically record transmittance or absorbance (ordinates) against wavelength or frequency (abscissae). Recording instruments are particularly useful in obtaining absorption spectra for identification purposes. Infrared spectrophotometers are generally of the recording type.

BEER'S LAW

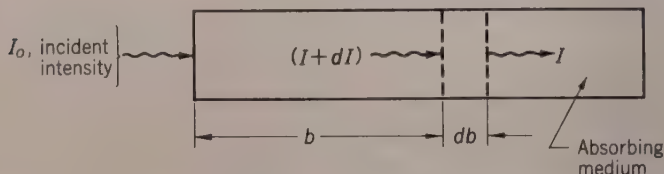
Derivation

(See Sec. 21B.2a, p. 511)

When light traverses an absorbing medium, the intensity is decreased. At any point, the decrease in intensity (dI) is proportional to the intensity (I) itself, and also to the length (db) of medium traversed.

In mathematical notation, using the symbolism defined in the following figure, this statement becomes

$$dI = -kI \, db \quad (Sa)$$



Equation *Sa* expresses a very frequently encountered law, known as the *law of growth or decay*. It describes the growth or decay of populations, radioactivity, money at compound interest, etc.

Separating variables, and integrating Eq. *Sa*, gives

$$\frac{dI}{I} = -k \, db \quad (Sb)$$

$$\log_e I = -kb + \text{constant} \quad (Sc)$$

If $I = I_o$ when $b = 0$, the integration constant can be evaluated, and Eq. *Sc* becomes

$$\log_e \frac{I}{I_o} = -kb \quad (Sd)$$

$$\log_{10} \frac{I}{I_o} = -\frac{kb}{2.303} \quad (Se)$$

Equation *Se* relates the intensity to the path length of medium traversed. The dependence of intensity upon concentration of an absorbing solute is not stated in Eq. *Se*, but was studied by Beer, who found that the proportionality constant, k in Eq. *Se*, is in turn proportional to the concentration, C , of the absorbing substance.

$$\frac{k}{2.303} = aC \quad (Sf)$$

Combination of Eqs. *Se* and *Sf* gives the logarithmic form of Beer's law, identical to Eq. 21.3 (p. 511).

$$\log_{10} \frac{I}{I_o} = -abC \quad (Sg)$$

Equation *Sg* is commonly called "Beer's law," even though it is recognized that Lambert, Bouguer, and others contributed independently to its formulation.

Extensions of Beer's Law

(See Sec. 21B.2c, p. 512)

As given in Eq. 21.3, Beer's law applies only for a single solute, and only for monochromatic light. However, the law may be properly extended to systems for which the light is not monochromatic, and also to systems containing more than one solute.

Apparent failure of Beer's law when the molar absorptivity varies with wavelength. Suppose that the absorbing solution is subjected to light of two different wavelengths, λ_1 and λ_2 .

Let: a_1 and a_2 be the molar absorptivities of the solute at wavelengths λ_1 and λ_2 , respectively.

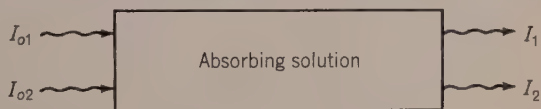
I_{o1} and I_1 be the incident and emergent intensities of light of wavelength λ_1 .

I_{o2} and I_2 be the incident and emergent intensities of light of wavelength λ_2 .

Equation 21.3 may be applied to the intensity at each wavelength.

$$I_1 = I_{o1}10^{-a_1bC} \quad I_2 = I_{o2}10^{-a_2bC} \quad (Sa)$$

The over-all or total intensities of the incident (I_{ot}) and emergent (I_t) beams are obtained by summing the component intensities.



$$I_{ot} = I_{o1} + I_{o2} \quad (Sb)$$

$$I_t = I_1 + I_2 \quad (Sc)$$

Substituting Eqs. Sa for I_1 and I_2 in Eq. Sc,

$$I_t = I_{o1}10^{-a_1bC} + I_{o2}10^{-a_2bC} \quad (Sd)$$

The total transmittance may be found from Eqs. Sd and Sb.

$$\frac{I_t}{I_{ot}} = \frac{10^{-a_1bC}[I_{o1} + I_{o2}10^{(a_1-a_2)bC}]}{I_{o1} + I_{o2}} \quad (Se)$$

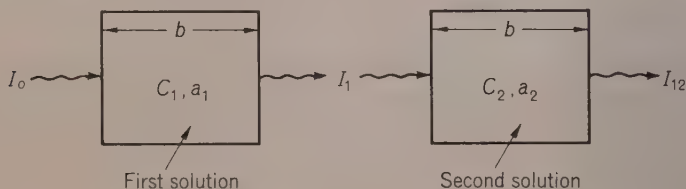
Converting Eq. Se to logarithmic form, we have

$$\log(I_t/I_{ot}) = -a_1bC - \log(I_{o1} + I_{o2}) + \log[I_{o1} + I_{o2}10^{(a_1-a_2)bC}] \quad (Sf)$$

It may be seen that $\log(I_t/I_{ot})$ is nonlinear in bC , which means that Beer's law is not obeyed for the total incident and transmitted intensi-

ties. It should be reemphasized, however, that Beer's law does hold for the intensity at each wavelength.

Dependence of transmittance upon composition when two absorbing solutes are present. Consider two solutions, each containing a single absorbing solute, the first solution being $C_1 M$ in a solvent with a molar absorptivity a_1 , and the second solution being $C_2 M$ in a solvent with a molar absorptivity a_2 . Monochromatic light is passed through these two solutions in series, as shown.



Let I_o be the intensity incident upon the first solution, and let I_1 be the intensity emergent from this solution and incident upon the second solution. Let I_{12} be the intensity emergent from the second solution. The path lengths through both solutions are assumed to be the same. Under these circumstances, Beer's law holds independently for each solution.

$$I_1 = I_o 10^{-a_1 b C_1} \quad I_{12} = I_1 10^{-a_2 b C_2} \quad (Sg)$$

Equations *Sg* may be combined to eliminate I_1 .

$$\frac{I_{12}}{I_o} = 10^{-a_1 b C_1} \cdot 10^{-a_2 b C_2} \quad \text{or} \quad \log \frac{I_{12}}{I_o} = -a_1 b C_1 - a_2 b C_2 \quad (Sh)$$

The argument is not altered if both solutes exist and absorb independently within the same solution, as long as there is no interaction between them.

In terms of absorbance,

$$A = \log \frac{I_o}{I} = a_1 b C_1 + a_2 b C_2 \quad (Si)$$

Equation *Si* gives the absorbance of the solution that contains the two solute species. It may be seen that absorbances of the individual solutes are additive.

Analysis of Mixtures of Two Absorbing Substances

(See Sec. 21B.4d, p. 521)

Suppose that two substances, A and B, absorb as shown in Fig. 21.4 (p. 522). Let $a_{A\lambda_A}$ and $a_{A\lambda_B}$ be the molar absorptivities of A at wave-

lengths λ_A and λ_B , respectively, and let $a_{B\lambda_A}$ and $a_{B\lambda_B}$ be the molar absorptivities of B at wavelengths λ_A and λ_B , respectively. Then, if Beer's law holds for both substances at both wavelengths,

At λ_A ,

$$A_{\lambda_A} = (a_{A\lambda_A})b[A] + (a_{B\lambda_A})b[B] \quad (Sa)$$

At λ_B ,

$$A_{\lambda_B} = (a_{A\lambda_B})b[A] + (a_{B\lambda_B})b[B] \quad (Sb)$$

The constants $(a_{A\lambda_A})b$ and $(a_{A\lambda_B})b$ may be determined by measuring the absorbances of a solution that contains a known concentration of A alone at the two wavelengths λ_A and λ_B ; and the constants $(a_{B\lambda_A})b$ and $(a_{B\lambda_B})b$ may be determined similarly on a solution of B alone. With these four constants known, measurement of the absorbances of the unknown solution at the two wavelengths allows calculation of [A] and [B] in the unknown solution from the two simultaneous equations *Sa* and *Sb*.

After the four constants are determined from measurements of known solutions of A and B alone, however, it is necessary to check the validity of the method by running known mixtures of A and B, to ascertain that Beer's law holds and that there is no interaction between A and B. A more detailed description, including the selection of conditions for best accuracy, is given in advanced works, along with empirical methods for analyzing two-color mixtures which do not obey Beer's law (**M14**, **P6**).

The same method may be applied to multicomponent systems. However, the accuracy is poor unless the spectra are quite discrete, as in the infrared region. In the infrared region analyses are routinely made of some mixtures with six components. Analyses of systems with as many as twelve components have been reported. Supporting determinations by other, independent methods of analysis almost always accompany the spectrophotometric determination when there are many components present.

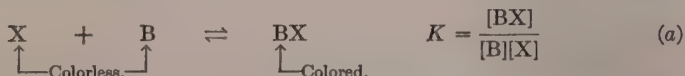
Effect of Chemical Equilibria on Beer's Law

(See Sec. 21B.4c, p. 518)

It should be clearly understood that the term C in Eqs. 21.3 and 21.4 (pp. 511, 514) represents the concentration only of the absorbing species. If the total concentration (C_t) of the sought-for substance is distributed among several solute species, then C is only a part of C_t . If the solute species that contain the sought-for substance are in equilibrium, then C is a function (not necessarily linear) of C_t , and the absorbance, A , is consequently also a function (not necessarily linear) of C_t . It is for this

reason that A may be taken as a measure of C_t , even though all the sought-for substance may not be converted to the absorbing form. The following two examples illustrate the nature of the relationship between A and C_t for two simple cases.

Example S1. Suppose that the sought-for substance X is nonabsorbing; and that for spectrophotometric determination X is converted only partially to a colored form BX by a controlled, large excess of reagent B , according to the equilibrium



Prove that the total concentration (C_t) of X is linearly related to the absorbance A .

If Beer's law holds for the colored species BX , then

$$A = ab[BX] \quad (b)$$

The total concentration of X is

$$C_t = [X] + [BX] \quad (c)$$

$$C_t = \frac{[BX]}{K[B]} + [BX] \quad (d)$$

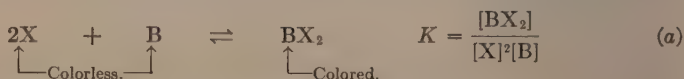
$$C_t = [BX] \left(1 + \frac{1}{K[B]} \right) \quad (e)$$

Eliminating $[BX]$ between Eqs. b and e gives

$$A = \frac{abC_t}{1 + (1/K[B])} \quad (f)$$

This example shows that the absorbance is proportional to C_t , even though X is not quantitatively converted to the colored form, provided that a , b , K , and $[B]$ are kept constant. The same conclusion holds even if X is distributed among several equilibria of type a .

Example S2. Suppose that the sought-for substance X is nonabsorbing, and that for spectrophotometric determination it is converted partially to a colored form (BX_2) by a large, controlled excess of reagent B , according to the equilibrium



Show how the absorbance is related to the total concentration (C_t) of X .

If Beer's law holds for the colored species BX_2 , then

$$A = ab[BX_2] \quad (b)$$

The total concentration of X is

$$C_t = [X] + 2[BX_2] \quad (c)$$

$$C_t = \sqrt{\frac{[BX_2]}{K[B]}} + 2[BX_2] \quad (d)$$

Equation *d* is a quadratic in $\sqrt{[BX_2]}$, and may be solved for $\sqrt{[BX_2]}$ by the quadratic formula, giving

$$\sqrt{[BX_2]} = \frac{1}{4} \left(-\frac{1}{\sqrt{K[B]}} + \sqrt{\frac{1}{K[B]} + 8C_t} \right) \quad (e)$$

Squaring Eq. *e* to obtain $[BX_2]$ and substituting in Eq. *b* gives

$$A = \frac{ab}{8K[B]} (1 + 4KC_t[B] - \sqrt{1 + 8KC_t[B]}) \quad (f)$$

This example shows that the absorbance is definitely (but not linearly) related to C_t and may be taken as a measure of C_t , even though X is not quantitatively converted to the colored form.

The same conclusion holds even if X is distributed among several equilibria. In order that the absorbance may be a measure of C_t , however, it is necessary that all reagent concentrations such as $[B]$ be kept constant, as well as all factors affecting the value of the equilibrium constant K .

FURTHER DETAILS ON QUALITATIVE ANALYSIS

(See Sec. 21B.3, p. 514)

Because the method is empirical, identification by an absorption curve is not regarded as certain, but only as indicative. Of course, the greater the wavelength range over which the known and unknown curves agree, and the more complex the curves are, the more the identification may be regarded as certain. But generally, unless the number of compounds that may be present in the unknown is quite restricted, some other independent test is applied to verify that the correct identification has been made. Such independent tests, based on other chemical or physical properties, are very useful and necessary when the unknown absorption curve closely resembles those for several known compounds. Because of the discreteness of infrared absorption spectra, they are particularly useful in qualitative analysis.

The greatest danger in a qualitative analysis is not that the worker will make an incorrect identification, but that he will fail to identify two materials as being identical because of differences in their absorption curves due to trivial differences in impurity contents. Thus a trace of a highly absorbing impurity (which may be of little or no chemical significance) may completely mask the absorption of the major component with which the impurity is mixed.

Techniques exist for the qualitative identification of mixtures of several components, but these are beyond the scope of this book. Again, the discrete infrared region is particularly useful in such analyses. In resolving mixtures, tests based on other properties of the substances usually accompany the spectrophotometric identification.

For qualitative analysis, spectral absorption data is often plotted as $\log A$ versus wavelength, rather than as A versus wavelength. From Eq. 21.4 (p. 514), it may be seen that A is dependent not only upon a , but also upon b and C . To facilitate comparison in qualitative identification, it is convenient to have the shape of the absorption curve dependent only upon the properties of the substance, and not dependent upon the concentration and cell dimensions.

By taking the log of both sides of Eq. 21.4, we obtain

$$\log A = \log a + \log b + \log C$$

Examination of this equation shows that b and C , which are constant for any one sample in any one cell, do not affect the shape of the $\log A$ curve, but simply shift it up or down, and the shape of the curve depends only on a . Comparison of curves taken in different cells at different concentrations is thereby simplified.

PRECISION SPECTROPHOTOMETRY

(See Sec. 21B.4c, p. 518)

In this section, an examination is made of the way in which instrumental errors affect the concentration calculated from transmittance measurements. A description is given of some high precision methods.

Optimum Transmittance for Minimum Instrumental Error

Because of the logarithmic relationship between concentration and transmittance, small errors in measuring the transmittance cause large relative errors in the calculated concentration at low and high transmittances. As a result, for the highest precision in determining concentrations, it is best to select conditions so that the sample has an intermediate transmittance. In this section, the dependence of the error in concentration upon the errors made in measurement of the transmittance is studied.

In making a spectrophotometric determination, the intensity of light transmitted through the solution is not measured directly, but rather a scale reading (R) is obtained that is in most instruments directly proportional to intensity.

$$I = kR + k' \quad (Sa)$$

Since the instrumental errors affect R , it is necessary to relate the concentration to the scale reading. This may be done with the integrated form of Beer's law for which the integration constant has not yet been determined (Eq. *Sc*, p. 870).

$$\log I = -abC + \text{constant} \quad (Sb)$$

Combination of Eqs. *Sa* and *Sb* to eliminate I gives

$$\log (kR + k') = -abC + \text{constant} \quad (Sc)$$

The constants in Eq. *Sc* are determined by the boundary conditions that in turn are established by working procedure. Thus, when $C = 0$, the sample cell is transparent, and the instrument is adjusted to give a scale reading, R_{100} , usually chosen as 100 scale divisions.

$$\log (kR_{100} + k') = \text{constant} \quad (Sd)$$

Also, when the photocell is darkened, to represent infinite concentration, the instrument is adjusted to give a scale reading, R_0 , usually chosen as zero scale divisions.

$$\log (kR_0 + k') = -\infty + \text{constant} \quad (Se)$$

From Eq. *Se*, $kR_0 + k' = 0$, or

$$k' = -kR_0 \quad (Sf)$$

Equations *Sd* and *Sf* may be used to evaluate the constants in Eq. *Sc*, giving the dependence of C upon scale reading.

$$\log \frac{R - R_0}{R_{100} - R_0} = -abC \quad (Sg)$$

$$C = -\frac{1}{ab} \left[\log (R - R_0) - \log (R_{100} - R_0) \right] \quad (Sh)$$

The error in C is caused by the errors in setting and reading R_0 , R , and R_{100} . For a good instrument and a skilled operator, there are no determinate errors; present evidence indicates that the errors in R_0 , R , and R_{100} (and therefore the error in C) are random, due to instrumental noise.

The standard deviation (c) of C may be calculated from the standard deviations (r_0 , r , and r_{100}) of R_0 , R , and R_{100} by the method on page 642.

$$c^2 = \left(\frac{\partial C}{\partial R_0} \right)^2 r_0^2 + \left(\frac{\partial C}{\partial R} \right)^2 r^2 + \left(\frac{\partial C}{\partial R_{100}} \right)^2 r_{100}^2 \quad (Si)$$

$$c^2 = \left(\frac{0.4343}{ab} \right)^2 \left[\frac{(R_{100} - R)^2 r_0^2}{(R - R_0)^2 (R_{100} - R_0)^2} + \frac{r^2}{(R - R_0)^2} + \frac{r_{100}^2}{(R_{100} - R_0)^2} \right] \quad (Sj)$$

The relative standard deviation of C may be found from Eqs. Sh and Sj .

$$\frac{c}{C} = \frac{0.4343 \sqrt{\frac{(R_{100} - R)^2 r_0^2}{(R - R_0)^2 (R_{100} - R_0)^2} + \frac{r^2}{(R - R_0)^2} + \frac{r_{100}^2}{(R_{100} - R_0)^2}}}{\log \left(\frac{R - R_0}{R_{100} - R_0} \right)} \quad (Sk)$$

For ordinary use, R_0 is set at zero scale units and R_{100} at 100 scale units so that Eq. Sk becomes

$$\frac{c}{C} = \frac{0.4343 \sqrt{\frac{(100 - R)^2 r_0^2}{10^4 R^2} + \frac{r^2}{R^2} + \frac{r_{100}^2}{10^4}}}{\log (R/100)} \quad (Sl)$$

The errors r_0 , r , and r_{100} are each complicated composites of the random errors in all parts of the instrument (variation in source intensity, variation in stray light, instability in the photocell-amplifier-meter system, etc.). They depend not only on the particular instrument, but also upon the working procedure by which the instrument is used. It would be hopelessly complicated to express r_0 , r , and r_{100} in terms of their common component errors. Instead, it is easier to evaluate each empirically from replicate measurements with the particular instrument and working procedure at hand.

For some instruments, such as infrared spectrophotometers with thermal detectors, the standard error is independent of the magnitude of R . In this case $r_0 = r = r_{100}$, and Eq. Sl becomes

$$\frac{c}{C} = 0.00614 \left(\frac{r}{R} \right) \frac{\sqrt{R^2 - 100R + 10^4}}{\log (R/100)} \quad (Sm)$$

Equation Sm may be differentiated with respect to R , or it may be plotted, to show that c/C is a minimum at $R = 38.8$ divisions, which represents the optimum reading region. In Fig. S21.3, curve I is a plot of Eq. Sm , r being taken as 1 division (i.e., 1% of full scale). Inspection of curve I shows that an instrumental error of 1 division causes a relative standard deviation of over 3% in C , even in the region of optimum transmittance, and much larger errors at low or high transmittances.

For many instruments, on the other hand, the standard error depends on the magnitude of R . As an approximation, a linear dependence may be assumed.

$$r = r_0 + pR \quad (Sn)$$

In this case, Eq. *Sl* becomes

$$\frac{c}{C} = \frac{0.4343 \sqrt{\frac{(100 - R)^2 r_0^2}{10^4 R^2} + \frac{(r_0 + pR)^2}{R^2} + \frac{(r_0 + 100p)^2}{10^4}}}{\log (R/100)} \quad (S_0)$$

In Fig. S21.3, curve II is a plot of Eq. *So*, with $r = 0.25 + 0.0075 R$.*

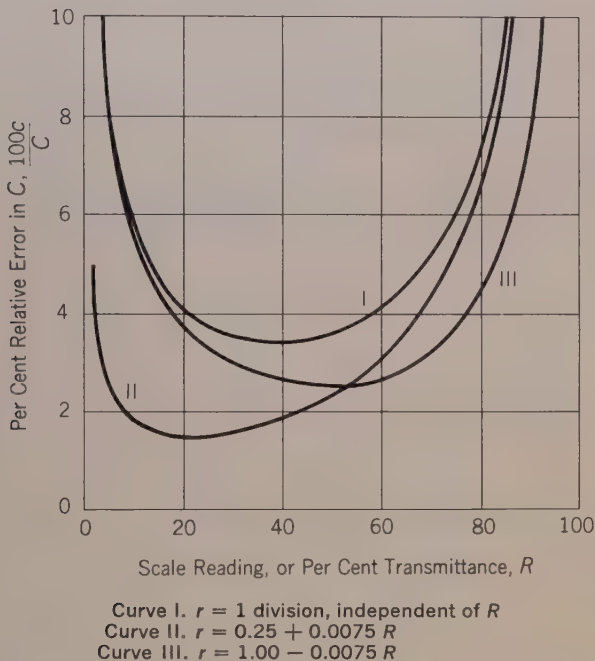


FIG. S21.3. Scale Ranges for Minimum Error in Measuring Concentrations with Various Kinds of Instruments—For all curves, instruments are calibrated to read zero divisions when the photocell is dark, and 100 divisions when the sample cell contains no absorbing solute.

Differentiation of the equation for curve II, or an examination of its plot, shows a minimum at 20.1 divisions, which marks the optimum reading region.

*In the plot of curve II, r_0 and p are chosen to give a standard deviation of 1 division at $R = 100$, and 0.25 division at $R = 0$. For these particular values of r_0 and p , curve II therefore lies below curve I at low scale readings. However, this does not permit the inference that an instrument with a variable standard deviation is better than an instrument with a constant standard deviation.

Curve III is another plot of Eq. S_0 , with $r = 1.00 - 0.0075 R$, which describes the error caused by an instrument having a larger standard deviation at $R = 0$ than at $R = 100$ divisions. The minimum comes at 49.8 divisions.

The conclusion that may be drawn from Fig. S21.3 is that the sample transmittance should lie in the range 20–60% (absorbance 0.2–0.7) for maximum precision on most instruments. Outside this range, the precision may be poor. In particular, the extremes of the scale should be avoided; if a sample transmittance falls below 10% or above 70%, another sample should be prepared to fall within the optimum transmittance range.

High Precision Spectrophotometric Procedures

There are *expanded scale* spectrophotometric procedures that give very high precision (**R4**). In these methods, the low end of the instrument scale ($R = 0$) is set with a high standard solution having a con-

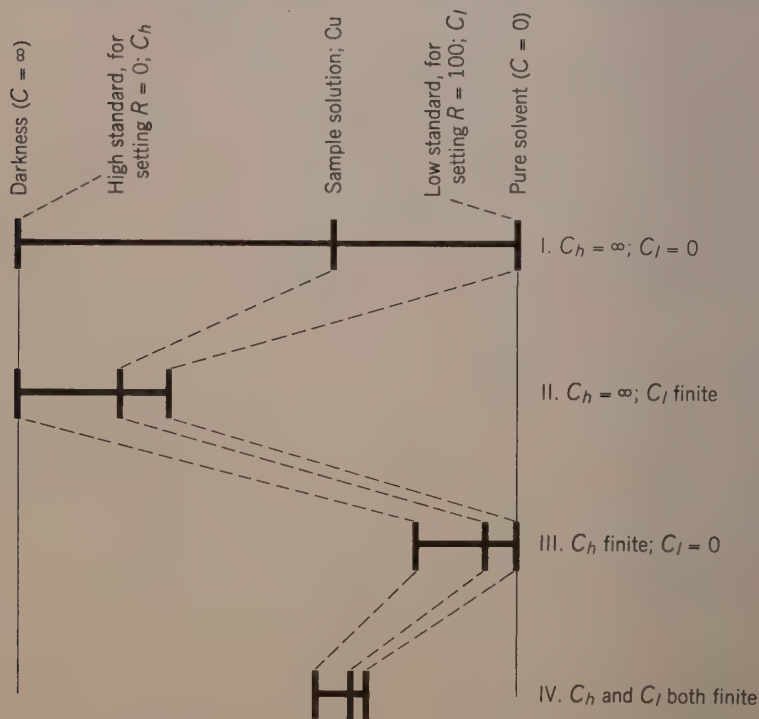


FIG. S21.4. Comparison of Spectrophotometric Procedures—Heavy horizontal lines represent the instrument scale from 0 to 100 divisions. Heavy vertical lines represent scale readings for sample and standard solutions.

centration (C_h) higher than that of the highest sample that is anticipated. The high end of the instrument scale ($R = 100$) is set with a low standard solution having a concentration (C_l) lower than that of the lowest sample solution that is anticipated.

The procedures differ in the concentrations (C_h and C_l) of the standard solutions that are used to calibrate the scale, as outlined in Fig. S21.4.

In the *ordinary procedure* (I), the instrument scale reading (R) is set to zero when the photocell is darkened (to represent infinite concentration), and is also set to 100 divisions with pure solvent in the sample cell (to represent zero concentration). In this case, the instrument scale from 0 to 100 divisions represents the concentration range from zero to infinity. As shown in the preceding section, passable precision can be obtained only for samples of intermediate absorbance. Samples with high or low absorbances cannot be precisely determined. At best, the ordinary procedure operates around the 1% error level.

In the *transmittance ratio procedure* (II), R is set to zero with the darkened photocell (to represent infinite concentration). The low standard, used to set R to 100, is slightly more dilute than the most dilute sample that is anticipated.

Procedure II is suitable for the measurement of highly absorbing solutions. Thus, suppose that a sample series lies in the 0–10% transmittance range (absorbance > 1). With procedure II, the 0–10% transmittance range is made to cover 0–100 scale units, as compared to 0–10 scale units with the ordinary procedure, providing a tenfold increase in precision over the ordinary procedure.

In order to use procedure II, the instrument must have enough reserve sensitivity so that full-scale response can still be obtained through the fairly concentrated low standard. Not all instruments have such reserve sensitivity. The additional sensitivity may be achieved by: (1) increased amplification of the photocell output, (2) increased slit width, (3) increased illumination. However, sensitivity cannot be increased without limit by any of these devices, for each is also accompanied by adverse effects.

In the *trace analysis procedure* (III), R is set to 100 with pure solvent in the sample cell (to represent zero concentration), and R is set to zero with a high standard solution having a concentration (C_h) somewhat higher than that of the most concentrated sample that is anticipated.

The trace analysis procedure is particularly suited to the measurement of dilute samples. Thus, suppose that a sample series falls in the 90–100% transmittance range (0–0.05 absorbance). With procedure III, this range can be made to cover 0–100 scale units, as compared to 10 units with the ordinary procedure, providing increased precision over the ordinary procedure.

In order to use procedure III, the instrument must have a *bucking circuit*, with which the response obtained with the high standard solution may be brought to $R = 0$. Most recorders have a zero adjustment sufficiently wide to permit such an adjustment.

In the *ultimate precision procedure* (IV), the low standard is chosen to be slightly more dilute, and the high standard to be slightly more concentrated than the samples to be measured. Procedure IV gives high precision for samples lying within a narrow concentration range. Thus, suppose that a set of samples lies in the 40–50% transmittance range (0.3–0.4 absorbance). The low standard of 50% transmittance is used to set R to 100, and the high standard of 40% transmittance is used to set R to zero. In this way, the 40–50% transmittance range covers 0–100 scale units, as compared to 10 units by the ordinary procedure.

Procedures II and III permit determinations at the 1% error level in regions of high and low transmittance, where the ordinary method is inapplicable. Procedure IV permits spectrophotometric determinations below the 0.1% error level, comparable to gravimetric and volumetric methods, providing that the instrument is stable and versatile enough to use with procedure IV.

High precision indirect procedures have also been classified, in which the sought-for substance reacts with a colored reagent to produce a bleaching effect (R5).

METHODS RELATED TO SPECTROPHOTOMETRY

(See Sec. 21D, p. 524)

Turbidimetry

When a light beam passes through a medium containing suspended particles, a part of the light is blocked out by each particle, and the emergent intensity is less than the incident intensity. It may be seen immediately that the transmittance is not simply related to the mass of suspended material per unit volume of medium (i.e., the mass concentration), but depends rather upon the number of light-blocking particles per unit volume and their cross-sectional areas, as the following example shows.

Example. Calculate the cross-sectional blocking area of 1.00 g of a solid (density, 2.00 g/cc), if the solid is distributed as a layer of spherical particles across a light beam, and if the particles have radii of (a) 10^{-2} cm, (b) 10^{-4} cm. (Assume that the layer is only one particle deep.)

(a) If each particle has a radius of 10^{-2} cm, the volume of a single particle is

$$\frac{4}{3}\pi(10^{-2})^3 = 4.19 \times 10^{-6} \text{ cm}^3$$

The number of particles in 1.00 g is

$$1.00 \left[\times \frac{1}{2.00} \right] \times \frac{1}{4.19 \times 10^{-8}} = 1.19 \times 10^5$$

$\underbrace{\hspace{10em}}_{\text{grams of blocking material}} \quad \underbrace{\hspace{10em}}_{\text{milliliters of blocking material}}$

The blocking area of 1.00 g is

$$\left(\text{Area of one particle} \right) \times \left(\text{number of particles} \right) = [\pi(10^{-2})^2][1.19 \times 10^5] = 37.4 \text{ cm}^2$$

(b) Similarly, if each particle has a radius of 10^{-4} cm, the blocking area of 1.00 g is

$$[\pi(10^{-4})^2] \left[\frac{1.00/2.00}{\frac{4}{3}\pi(10^{-4})^3} \right] = 3.74 \times 10^3 \text{ cm}^2$$

It is apparent that the more finely divided material blocks the light more effectively.

For different samples, the transmittance may be taken as a measure of the mass of suspended material per unit volume only when the particle size of the suspended material is the same in all samples. The measurement and use of transmittance to determine the amount of suspended material is called *turbidimetry*.

The mechanism of light diminution in the foregoing example is oversimplified. A more careful analysis shows that the transmittance has approximately the same form as Beer's law. That is,

$$\log \frac{I}{I_0} = -k_t b C \quad (Sa)$$

The constant k_t is a proportionality constant bearing no relation to the absorptivity of Eq. 21.3 (p. 511), and is dependent upon particle size and shape, refractive indices of the suspended and suspending media, and wavelength. The symbol C is the *mass concentration* of the suspended material, and may be expressed in any concentration unit (i.e., molarity) even though the material is not in true solution. In real cases there are departures from Eq. *Sa*, just as there are departures from Beer's law.

Turbidimetric procedures are considerably less accurate than ones in which light is absorbed by a homogeneous solution, the chief source of error being failure to obtain reproducible and stable suspensions. Gum arabic or gelatin is often used to stabilize the suspensions.

Most spectrophotometers may be used without modification for turbidimetric measurements. For an analysis, the sought-for substance is precipitated with an excess of a precipitating agent, under very care-

fully controlled conditions to ensure uniform particle size. The ratio I/I_o may be measured with a spectrophotometer, or the suspension may be compared visually with a standard suspension. It is not necessary that Eq. *Sa* hold if the method of the working curve is used, or if a match is made to a standard suspension.

Turbidimetric determinations may be performed quite simply, and are often used when high precision is not required. Methods for the following substances are typical of many that are in the literature: Ca (as oxalate or oleate), SO_4 (as BaSO_4), and Zn (as ferrocyanide). Organic substances are also determined turbidimetrically; for example, nicotine may be precipitated with tungstosilicic acid. The growth of the assay organisms in biological assays is often measured turbidimetrically.

Nephelometry

When a light beam passes through a medium containing suspended particles, a part of the light is scattered. That is, a light ray impinging upon a suspended particle may be reflected in a direction different from that of the impinging beam. The intensity of the scattered light (I_s) is not a function of the mass concentration of the suspended particles alone, but depends rather on the number of particles per unit volume and on the particle size. Just as in turbidimetry, I_s/I_o may be taken as a measure of the amount of suspended material per unit volume only when the particle size of the suspended material is the same for all samples compared. The measurement and use of I_s/I_o to determine the mass concentration of suspended material is called *nephelometry*. The nephelometric process is outlined in Fig. S21.5.

To convert a colorimeter or spectrophotometer to a nephelometer, only a slight modification is necessary; it must be possible to view the

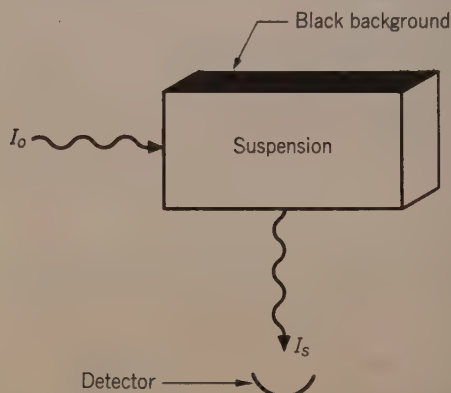


FIG. S21.5. Nephelometric Method of Analysis

sample cell at right angles to the incident beam. Most instruments are so designed. Nephelometric procedures require the same careful control of conditions as turbidimetric procedures.

Where it may be used, the nephelometric procedure is helpful in the determination of low concentrations of sought-for material. In such a case the turbidimetric measurement is unprecise because only a small difference in intensity between I and I_o must be measured at high levels of illumination. Nephelometric (and fluorimetric) procedures do not suffer from this disadvantage because I_s is observed at right angles to the incident beam, which does not reach the detector.

The scattered intensity I_s is a highly complicated function of the properties of the scattering suspension. Rayleigh has presented a theory of scattering by small particles, but this does not apply to most systems of chemical interest except in a qualitative way. More rigorous theories of scattering exist (Y1). In general, for a given mass of scattering material, the efficiency of scattering increases as wavelength decreases. (Thus if the suspension is illuminated with white light, the scattered light contains a higher proportion of blue and the transmitted light a higher proportion of red.) In addition, I_s depends upon the angle between the incident and observed light beams, the refractive indices of the media, and the size and shape of the particles. Therefore, if I_s/I_o is to be taken as a measure of the mass concentration of the suspended phase, very careful control is required. Since no simple relationship exists between I_s/I_o and the mass concentration of the scattering particles, it does not particularly matter what function of I_s/I_o is used to construct working curves. Often $\log I_s/I_o$ is used, not because of any theoretical significance, but to conform with spectrophotometric and turbidimetric methods.

As with turbidimetric procedures, the chief limitation on precision is the difficulty of obtaining reproducible and stable suspensions. Nephelometric determinations may be performed simply, and are used occasionally when high precision is not required. Methods for the following substances are representative of some that are in the literature: F (as CaF_2), Ag and Cl (as AgCl), Ba and SO_4 (as BaSO_4), and alkaloids (as phosphomolybdates).

Fluorimetry

Some substances fluoresce—that is, the molecules absorb light energy, and then reemit a part of this energy as light instead of dissipating it all as heat. The reemitted (fluorescent) light has a lower energy and a higher wavelength than the incident light. The intensity of the fluorescent light (I_f) may be taken as a measure of the concentration of the

fluorescing material. Since the fluorescent light is nondirectional, it may be observed at right angles to the incident beam, so that the latter does not interfere. Furthermore, since fluorescent light is of a different (i.e., higher) wavelength than the absorbed light, it is possible to irradiate the sample with monochromatic light and to observe the fluorescent light through a filter that passes the fluorescent light but not the incident light. Figure S21.6 outlines the fluorimetric method of analysis.

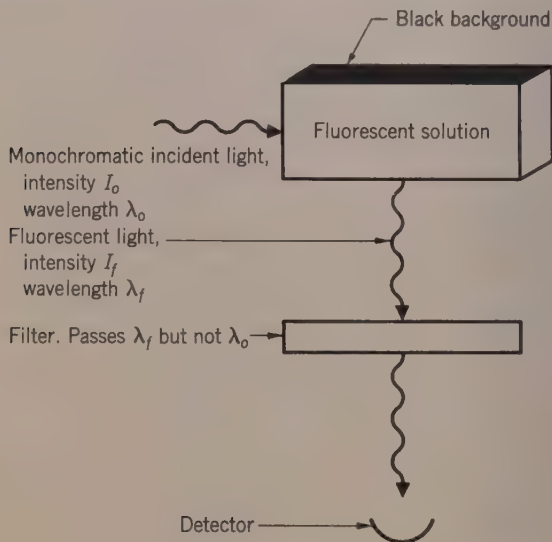


FIG. S21.6. Fluorimetric Method of Analysis

For solutions which absorb only slightly, so that I_o is not greatly reduced by absorption in passing through the cell, I_f/I_o is nearly a linear function of C for a particular instrument (U1).

$$I_f/I_o = k_f C$$

It is therefore advantageous to plot I_f/I_o versus C for the working curve, rather than $\log I_f/I_o$. The constant k_f depends upon the properties of the instrument as well as on the properties of the system.

A fluorescent substance possesses both an activation spectrum (because not all wavelengths are equally effective in producing fluorescence) and a fluorescence spectrum. The technique is therefore exceedingly useful for identification, or for the measurement of one substance in the presence of another. Further, the technique is very sensitive, some substances fluorescing strongly enough to be measurable at $0.01 \mu\text{g/ml}$. For example, less than $0.001 \mu\text{g}$ of Be may be detected as its colloidal,

fluorescent complex with the dye, morin, and amounts of the order of $0.1 \mu\text{g}$ may be determined with a standard deviation of 1%. Similarly, as little as $0.001 \mu\text{g}$ of U may be determined by its fluorescence in a melt of NaF.

Almost all inorganic substances and many organic ones do not fluoresce at room temperature in aqueous solution. However, many of these substances are determinable indirectly, either through their reaction with a fluorescent reagent, or through their reaction to form a fluorescent product. There are correlations between molecular structure and fluorescence (U1). Table S21.1 summarizes conditions for the determination of a few substances.

Of course, simplicity is not concomitant with so sensitive a procedure; there are complications and experimental difficulties that must be met for accurate results: (1) The solvent or impurities in it and other reagents may fluoresce. (2) Chemically inert substances may have a great effect

TABLE S21.1
SOME FLUORIMETRIC DETERMINATIONS

COMPOUND	MEDIUM	WAVELENGTH, $\text{m}\mu$	
		For Maximum Activation	Of Maximum Fluorescence
Al-alizarin garnet R...	Acetate buffer (pH 4.6)	435	560
Al-morin.....	Acetate buffer (pH 4.6)	425	515
Zr-flavanol.....	0.02 N H_2SO_4	250, 390	465
Anthracene.....	Cyclohexane	355	380, 400, 425
		375	450
Tyrosine.....	Phosphate buffer (pH 8)	275	320
Tryptophan.....	1 N Na_2CO_3	280	360
Indoleacetic acid.....	0.01 N HCl	275	360
Serotonin.....	Formate buffer (pH 4)	295	335
	3 N HCl	295	335, 550
Epinephrine and norepinephrine.....	0.1 N H_2SO_4	295	335
Aureomycin.....	1 N NH_3	335	445
Quinine.....	0.1 N H_2SO_4	250, 350	450
Reserpine.....	1 N H_2SO_4	385	500
Salicylic acid.....	0.1 N H_2SO_4	310	440
Estradiol.....	Conc. H_2SO_4	440	490

Data taken from Bulletin 2336-B (March, 1962), American Instrument Co., Inc., Silver Spring, Maryland, Table I, with permission of the publisher.

on fluorescence, either by absorbing the fluorescent light after emission, or by preventing the fluorescence from occurring. (3) Occasionally the fluorescent substance is destroyed by the absorption of the radiation, especially if ultraviolet light is used. In such cases I_f decreases as irradiation proceeds, and special techniques must be used for measurement.

Fluorimetric assays have received considerable impetus over the last decade, owing principally to the development of instruments.

Colorimetry

If there are no colored interferences, a colored substance may be determined by comparing its color with that of a standard solution of the sought-for substance. Instruments used to make such comparisons are called *color comparators* or *colorimeters*.

All colorimeters operate on the same principle. The standard and

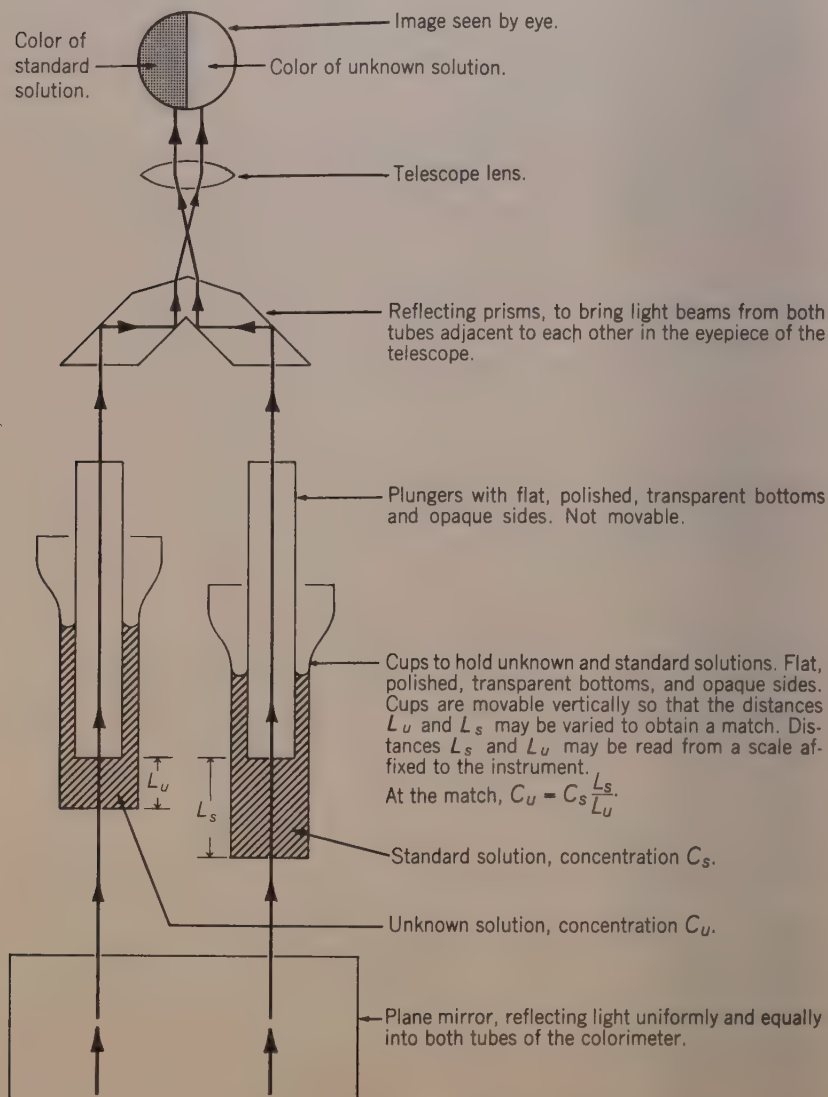


FIG. S21.7. The Duboscq Colorimeter

unknown solutions are placed in identical transparent containers, which in turn are placed in identical incident light beams. (Usually, white light is used, but colored light may also be used.) The concentration and/or thickness of the standard solution is varied until its color matches that of the unknown solution. When such a match is obtained, the amounts of colored substance in the volumes traversed by the light beams are assumed to be the same in both the standard and unknown solutions. This allows computation of the amount of sought-for substance in the unknown solution from the known amount in the standard. One of the more frequently used procedures for making the match involves use of the *Duboscq colorimeter*, whose construction and operation are summarized in Fig. S21.7.

It is generally true that whatever may be done with a colorimeter may be done more accurately with a spectrophotometer. The spectrophotometer has several advantages over the colorimeter. (1) By restricting the light to the wavelength region of maximum absorption, maximum sensitivity is obtained. (2) By restricting the light to the wavelength region where other interfering substances absorb least, high selectivity may be obtained. The spectrophotometer often allows analysis of multicomponent colored systems, but the colorimeter is useful for only one colored component. (Interference by a second color may sometimes be overcome in a colorimeter by the use of a filter, or by carrying out the color comparison with a standard solution containing the same amount of colored interference as the unknown solution. However, these methods are limited.) (3) Eye fatigue and partial color blindness often cause severe trouble in routine colorimetric matching procedures, but are of no consequence when a spectrophotometer with a photoelectric cell is used. (4) Finally, the continuous use of standard solutions is not necessary, once the spectrophotometric working curve has been established, whereas such standard solutions, or artificial standards, must always be used for color-matching procedures.

SUPPLEMENTARY QUESTIONS

Section 21B

S1. A solution contains two solutes, one of which absorbs at 400–435 $m\mu$, and the other of which absorbs at 500–560 $m\mu$. Describe how the color depends upon the composition.

S2. Onto Fig. S21.2 (p. 869), draw the sensitivity curve for the human eye (M14).

S3. Give a specific case in which light energy absorbed by a chemical system is (a) used predominantly to raise the temperature of the system; (b) used partly to bring about a chemical reaction in the system; (c) partly reemitted as light. For each case discuss the suitability of the phenomenon for development into an optical method of analysis.

S4. Describe how a double beam spectrophotometer reduces error due to instrumental drift and fluctuations.

S5. A colorless solution is transparent to all visible wavelengths. If the transmittance of a colorless solution is adjusted to 100% at a particular wavelength, why does the spectrophotometer reading change when the wavelength is changed?

S6. Draw a schematic diagram for a particular make of spectrophotometer. Give briefly the function and description of each of the following parts: light source, light-dispersing element, absorption cell, photocell, and measuring system.

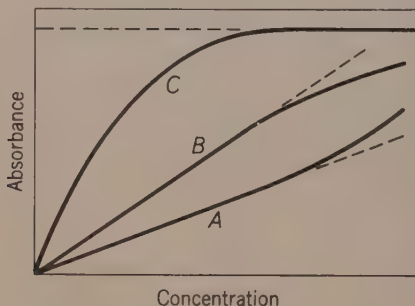
S7. On Fig. 21.4 (p. 522), there is a particular wavelength at which a single absorbance measurement will give the total concentration (i.e., sum of the molar concentrations) of both A and B. Specify this wavelength, and formulate an illustration in which an absorbance measurement at this wavelength would be analytically useful.

S8. A mixture of substances A and B (Fig. 21.4) is to be spectrophotometrically analyzed by absorbance measurements at two wavelengths. Specify the two wavelengths that should be chosen for each of the following types of mixtures: (a) the concentrations of A and B are about the same; (b) the concentration of A is considerably greater than that of B; (c) the concentration of A is considerably less than that of B.

S9. A colorless sought-for substance X is converted only partially by a large, controlled excess of colorless reagent B to a colored product X_2B for spectrophotometric determination. Draw approximately the working curve that shows how the absorbance varies with the total concentration of X.

S10. Answer Ques. S9 if the colored compound is XB_2 .

S11. Not all working curves are straight lines. For each of the working curves shown in the accompanying figure, speculate on the nature of the equilibria that involve the sought-for substance and other substances in solution.



S12. A simple acid-base indicator (HIn) has an acid ionization constant of 10^{-5} . Give the pH ranges over which the absorbance of a solution of the indicator is independent of pH, within an error of 1%.

S13. Consider the equilibria involving Cr(VI) (Appendix VIIA), and explain why a solution of $K_2Cr_2O_7$ around pH 6 apparently does not follow Beer's law (i.e., absorbance vs. total concentration is not a straight line). Would Beer's law be obeyed at high pH? Low pH?

S14. Not all instruments have enough reserve sensitivity to permit the use of the transmittance ratio method (II). Explain some ways in which the sensitivity may be increased for a particular instrument, and discuss the limitations of each way.

Section 21D

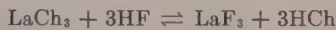
S1. Consult the literature, and outline an example of each of the following kinds of determinations: (a) colorimetric, (b) spectrophotometric, (c) turbidimetric, (d) nephelometric, (e) fluorimetric, (f) one in which the sought-for substance is itself the absorbing one, (g) one in which the sought-for substance is converted to the absorbing one, (h) one in which the sought-for substance alters the absorption of another substance. Describe methods not mentioned in this book.

S2. For a common element, consult the literature and outline a spectrophotometric method not described in this text.

S3. Devise a spectrophotometric method, based only on your chemical knowledge, for the determination of traces of Zn at concentrations around $10^{-5} M$ in pure water.

S4. As specifically as possible, tell how to perform the turbidimetric determination of Cl^- as AgCl , with special attention to those factors requiring close control. After describing the conditions, check with the literature.

S5. An indirect spectrophotometric method for low fluoride concentrations has been reported (F2). The fluoride sample solution is shaken with insoluble lanthanum chloranilate (LaCh_3), which is metathesized:



The absorbance of liberated chloranilic acid (HCh) is measured at $525 \text{ m}\mu$, where chloranilate ion does not absorb. (a) Recognizing that chloranilic acid is a weak acid, explain the importance of pH regulation, telling what happens if the pH is too high or too low. (b) Explain how a cationic impurity like Fe(III) would interfere. (c) Explain how an anionic impurity like $\text{PO}_4^{=}$ might interfere.

S6. In the spectrophotometric determination of Cu(II) with dithizone, Beer's law is followed, and the absorbance vs. copper concentration curves are linear, if a spectrophotometer is used at 510 or $625 \text{ m}\mu$. However, when a filter photometer is used, the absorbance vs. concentration curves are not always linear. Explain.

S7. Explain why the simple colorimetric method is not usable when more than one colored substance is present.

S8. Describe briefly an experimental test that would ascertain whether or not the equation in Fig. S21.7 (p. 888) is valid.

SUPPLEMENTARY PROBLEMS

Section 21B

S1. The molar absorptivity of a substance X is 3.50×10^3 at a particular wavelength. A solution containing an unknown concentration of X and another absorbing substance Y has a transmittance of 37.0% in a 1.00-cm cell at the given wavelength. A standard solution containing $2.00 \times 10^{-4} M$ X and the same concentration of Y as the unknown solution has a transmittance of 18.5%. What is the concentration of X in the unknown solution? *Ans.* $1.14 \times 10^{-4} M$.

S2. A sample solution contains both dichromate and permanganate. At $500 \text{ m}\mu$, the absorbance is 0.688 in a particular cell. The permanganate is then decolorized with KNO_2 , leaving the dichromate, and the absorbance falls to 0.306. A standard permanganate solution ($10.0 \mu\text{g Mn/ml}$) has an absorbance of 0.310, while a standard dichromate solution ($200 \mu\text{g Cr/ml}$) has an absorbance of 0.492. Calculate the Mn and Cr concentrations in the sample solution. With the help of Fig. 21.5 (p. 529), outline a more precise procedure for obtaining the Mn and Cr concentrations.

S3. In Prob. S2, all absorbances are measured in a spectrophotometer that is calibrated to give zero absorbance for distilled water. If the spectrophotometer were calibrated to give zero absorbance for the decolorized solution, what would be the absorbance of the sample solution? If only the Mn content were desired, outline a simpler procedure than that of Prob. S2. *Ans.* 0.382.

S4. The colorless substance X at low concentrations may be determined spectrophotometrically by adding a large excess of the colorless reagent Y, and then measuring the absorbance of the colored complex XY, which follows Beer's law.

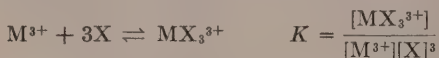


A standard solution containing total concentrations of $1.00 \times 10^{-5} M$ X and $0.00100 M$ Y has an absorbance of 0.575. An unknown solution containing X is made $0.00600 M$ in Y, after which the absorbance is .403. What is the X concentration in the unknown solution?

S5. One-millimole portions, each of a weak acid (HA) and its salt (NaA), are dissolved in one-liter volumes of various buffer solutions. The absorbances of the resulting solutions are measured at $650 m\mu$ in 2.00-cm cells and found to be: 0.950 (pH 12.00), 0.950 (pH 10.00), 0.677 (pH 7.00), 0.000 (pH 2.00), 0.000 (pH 1.00). Calculate the molar absorptivities of HA and A^- , and find K_a .

Ans. $a_{HA} = 0$; $a_{A^-} = 238 \text{ (moles/l)}^{-1} \text{ (cm)}^{-1}$; $K_a = 2.5 \times 10^{-7}$.

S6. A metal ion (M^{3+}) and a complexer (X) react as follows:



A solution containing $2.00 \times 10^{-4} M$ $M(ClO_4)_3$ and $0.100 M$ X gives an absorbance of 0.600 at $525 m\mu$ in a 1.00-cm cell. When the concentration of X in the solution is increased to $0.500 M$, the absorbance increases to 1.200. At $525 m\mu$, X is colorless, and the molar absorptivity of M^{3+} is 15. Calculate K and the molar absorptivity of MX_3^{3+} .

S7. A solution contains a colored substance (X) and a colorless one (Y). A colorless reagent (L) reacts quantitatively with Y to form a colored compound (YL), but does not react with X. The molar absorptivities of X and YL are 250 and $3.40 \times 10^3 \text{ (moles/l)}^{-1} \text{ (cm)}^{-1}$. A 10.00-ml portion of the solution is diluted to 250 ml, and the diluted solution gives an absorbance of 0.532 in a 2.00-cm cell. Another 10.00-ml portion is also diluted to 250 ml after addition of excess L, and the absorbance of the diluted solution is 0.975 in the 2.00-cm cell. Calculate the concentrations of X and Y in the original solution. *Ans.* $0.0266 M$ X and $0.00163 M$ Y.

S8. Show that Eq. S*f* (p. 871) reduces to Beer's law when $a_1 = a_2$.

S9. Solve Eqs. S*a* and S*b* (p. 873) explicitly for [A] and [B]. For high precision, show that the ratios of the molar absorptivities of A and B should be greatly different at the two wavelengths chosen for measurement.

S10. Suppose that 90% of the incident light ($0.90 I_o$) passes once through a cell containing an absorbing solution, and that most of the remaining 10% is lost by reflection. Suppose, however, that some of the reflected light (amounting to $0.01 I_o$) is reflected from the front and back windows of the cell, traversing the cell three times before rejoining the main emergent beam that passes on to the photocell. Show that Beer's law is apparently not followed in this case, that is, that the total emergent intensity is not linearly related to concentration.

S11. Prove that the following statement is not always correct. "If colorless A can be determined with colorless reagent B to form a colored product, and if the

working curve of absorbance vs. total A concentration is a straight line, then B can be determined with A as a reagent, and the working curve of absorbance vs. total B concentration is also a straight line." (Hint: Consider the case in which the product is AB₂.)

S12. What conclusion may be drawn if the shape of the log *A* (i.e., log log *I*/*I*₀) vs. wavelength curve is not independent of concentration?

S13. If the instrumental error is constant (*r* = 2 divisions), estimate the relative error in concentration when *R* is (a) 80 divisions, (b) 40 divisions. (Hint: Rather than calculate the error from Eq. *Sm*, p. 878, estimate the error from Fig. S21.3, p. 879.)

Ans. (a) 14.6%; (b) 6.8%.

S14. Calculate enough points on the error curve I in Fig. S21.3 to show that it passes through a minimum at *R* = 38.8 divisions.

S15. With the differential calculus, show that *c*/*C* in Eq. *Sm* (p. 878) is a minimum at *R* = 38.8 divisions.

S16. Show that for curve II in Fig. S21.3 Eq. *So* (p. 879) becomes

$$\frac{c}{C} = \frac{0.553}{100R \log(R/100)} \sqrt{R^2 + 15.4R + 770}$$

Use this equation to verify that *c*/*C* is a minimum at *R* = 20.1 divisions.

Section 21D

S1. In Fig. S21.6 (p. 886), assume that *I*₀ is appreciably diminished by absorption in passing through the cell, according to Beer's law. Derive an expression for the dependence of *I*_f/*I*₀ upon *C*, assuming that the fluorescent light is not appreciably absorbed.

Ans. $I_f/I_0 = K(1 - 10^{-abc})$.

S2. Plot *I*_f/*I*₀ as a function of *C*, using the relationship derived in Prob. S1. Assume that *K* = 0.01, and that *ab* = 1000 (moles/l)⁻¹. Discuss the dependence of *I*_f/*I*₀ on *C* as *C* becomes very small and very large.

S3. Assume that Cu(II) forms the complex CuD₂ quantitatively when an excess of dithizone (HD) is added, according to the equation



Let *C*_c and *C*_d be the total concentrations of Cu(II) and of dithizone, respectively, and let *a*_c and *a*_d be the molar absorptivities of CuD₂ and of HD, respectively. Show that

$$A = a_d b C_d + (a_c - 2a_d) b C_c$$

which is linearly dependent on *C*_c if *C*_d is controlled.

S4. Find the dependence of *A* upon *C*_c (Prob. S3) if conversion of Cu to the complex is not complete. State what variables would have to be controlled in order to determine Cu with dithizone in such a case.

S5. The molar absorptivity of the Cu(II)-dithizone complex is about 5 × 10⁴ in carbon tetrachloride at 545 mμ. If 0.005 absorbance unit is just detectable above the noise level of the spectrophotometer, what is the smallest concentration of Cu(II) that is detectable in a 1-cm cell?

Ans. 1 × 10⁻⁷ M.

S6. A 50.00-ml portion of a 0.0100 M FeCl₃ solution with an absorbance of 0.219 is mixed with a 25.00-ml portion of 0.00100 M CuCl₂·6 M HCl having an absorbance of 0.157. (a) What is the absorbance of the resulting solution, assuming that Beer's law is obeyed? (b) Suppose that the actual absorbance of the mixture is 0.389. Speculate on a reasonable explanation for the difference.

S7. A 10.00-ml portion of an unknown solution is treated and diluted to give 250.0 ml of a colored solution. Comparison of this diluted colored solution in a Duboscq colorimeter with a similarly prepared standard solution containing $2.5 \mu\text{g/ml}$ of the sought-for substance gives a match when L_u is 32.3 mm and L_s is 33.8 mm. What is the concentration of sought-for substance in the original 10.00-ml portion?

Ans. $65 \mu\text{g/ml}$.

S8. A 1.00-g sample of a concentrated solution of CuSO_4 is diluted with water to 100.0 ml in a volumetric flask. A 10.00-ml portion of this diluted solution is placed in a 250-ml volumetric flask; the $\text{Cu}^{2+}\text{-NH}_3$ complex color is then developed with an excess of conc. NH_3 , and the contents are diluted to volume. This solution is compared in a Duboscq colorimeter with a standard solution prepared by putting 25.00 ml of a solution containing $2.5 \text{ mg CuSO}_4/\text{ml}$ into a 250-ml volumetric flask, adding excess conc. NH_3 , and diluting to volume. At the match, L_s is 9.0 mm, while L_u is 46.0 mm. (a) What is the weight percentage of CuSO_4 in the original sample? (b) Why should the answer of part a be regarded only as an approximation? Describe a method of making the dilutions (of either standard or unknown) to allow a better estimation.

S9. Consider carefully the properties of the two solutions that are identical when a match is obtained with a Duboscq colorimeter. For the concentration and path length that exist for each solution at the match, would I/I_o as measured with a spectrophotometer be the same for both solutions? In such a case, show how Beer's law (Eq. 21.3) leads to the colorimetric relationship given in Fig. S21.7.

INSTRUMENTAL METHODS OF CHEMICAL ANALYSIS

POTENTIOMETRIC DETERMINATION OF CHLORIDE

(See Exp. 22.1, p. 550)

Construction of Equipment

Electrodes. Figure S22.1 gives details on the construction of the Ag-AgCl electrodes. Deposition of the AgCl coating (i.e., chloridization) is simple. The unchloridized Ag electrode and a small platinum electrode are connected as shown in Fig. S22.2, and are immersed in 0.1 *M* HCl. The resistance should be set to a maximum before immersion and then decreased to give a current density of 1–2 ma/cm². An adherent coating of AgCl is formed on the anode, and hydrogen is liberated at the cathode. Chloridization is adequate in 10–15 minutes, after a definite and visible coating of AgCl is formed. The color of the deposit may vary from whitish to plum gray, depending on chloridization conditions and the age and treatment of the deposit.

The electrodes last indefinitely unless they are roughly handled, or allowed to dry. If the asymmetry potential rises above 1 mv, the old

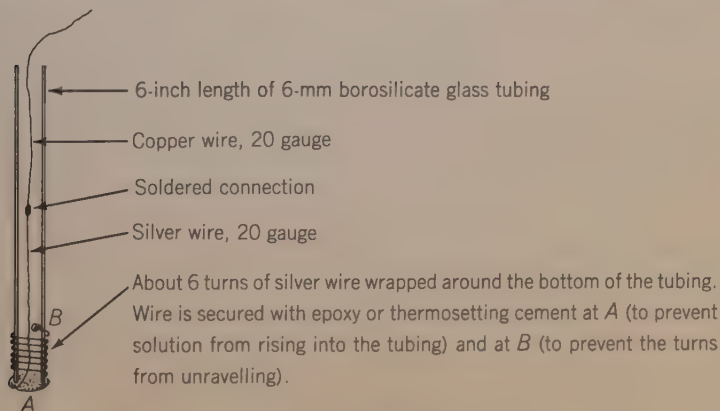


FIG. S22.1. Ag-AgCl Electrode

coating should be removed by immersion in 4 M NH_3 , followed by a water rinse. Before rechloridization, the electrode should be immersed briefly in 1 M HNO_3 and rinsed with water. The equipment of Fig. S22.2 should be made available, so that students may perform the chloridization if it becomes necessary.

Bridge. The bridge is made from 6-mm borosilicate glass tubing, to the dimensions shown in Fig. S22.3. The arms are filled to the level shown with 400-mesh Microbeads* and tamped down. To sinter the

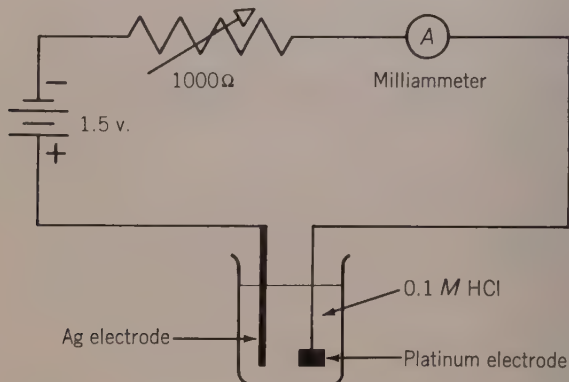


FIG. S22.2. Apparatus for Chloridization of Ag Electrodes

Microbeads, the bridge is laid flat on a sheet of stainless steel or brass that is raised slightly above the floor of a muffle furnace. The muffle controller should be set to 680°C , the furnace should be turned on, and then left on for an hour after the controlling temperature is reached.

After sintering, the bridge should not be taken immediately from the furnace; instead it should be allowed to cool slowly overnight in the closed furnace, so that proper annealing may occur. This process is sufficient to sinter the soft glass Microbeads, but not sufficient to melt the borosilicate glass tube. After sintering, the closed ends of the arms are cut off with a glass saw. Some experimentation may be needed to find the proper sintering temperature, which may vary with the furnace. If the sinter is very crumbly, a higher sintering temperature should be tried. If the sintering temperature is too high, the sinter may crack away from the tube walls, or the tube may crack, in which case a lower sintering temperature should be tried.

Assembly. The bridge and two Ag-AgCl electrodes (before chloridization) may be mounted on a small board, as shown in Fig. 22.5 (p. 553).

*Microbeads, Inc., 2505 Albion St., Toledo 6, Ohio.

Mounting may be performed with small straps or with epoxy cement. A short length of $\frac{3}{8}$ -inch iron rod should be fixed perpendicularly to the back of the board at its center, so that the assembly may be clamped onto a ringstand.

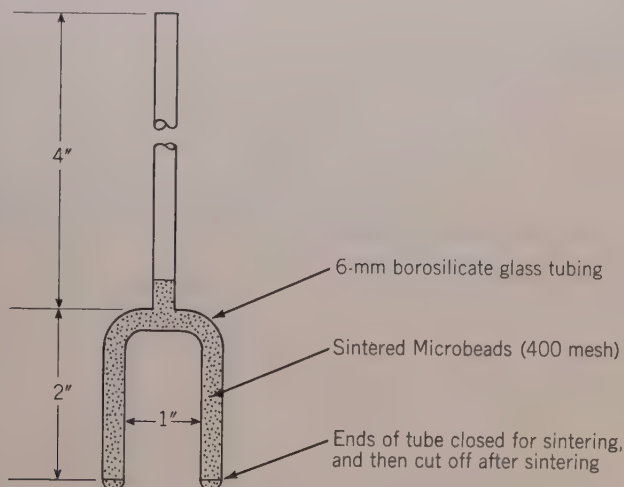


FIG. S22.3. Bridge

Measurement of Low Chloride Concentrations (B14, S28)

Two complications arise in attempting to extend the method of Exp. 22.1 to the measurement of chloride concentrations below $10^{-4} M$. One complication is caused by chloride impurities in the reagents, and the other by the solubility of AgCl . At low concentrations, AgCl may contribute as much as the sample to the total concentration of chloride in the measured solution. The contribution of AgCl cannot be treated simply by running a blank or control determination, because the solubility of AgCl depends on the chloride concentration of the sample, and varies with sample size in a way that is determined by the solubility-product relationship. For low chloride concentrations, therefore, Eq. 22.5 does not apply, and a different relationship must be derived.

Let K_s be the apparent solubility product of AgCl in the measured solution. If the ionic strength is controlled in the measured solution by making it high in an inert electrolyte (like the $0.1 M \text{H}_2\text{SO}_4$ of Exp. 22.1), then K_s is constant and independent of sample size.

The total chloride concentration in the measured solution is a sum of three parts: the chloride contributed by the sample ($X M$), the blank

contributed by the reagents ($B\ M$), and the chloride contributed by the solubility of AgCl ($S\ M$). These quantities are related through the solubility product:

$$S(X + B + S) = K_s \quad (Sa)$$

Likewise, in a standard solution of known concentration (A), the solubility-product principle still holds, even though the solubility of AgCl ($S'\ M$) is different from that in the sample solution.

$$S'(A + B + S') = K_s \quad (Sb)$$

If the voltage (V) is measured between the sample and standard solutions by the technique of Exp. 22.1, then V may be expressed as a function of concentrations by the same sort of reasoning that leads to Eqs. 22.4 and 22.5.

$$V = 0.0591 \log \frac{(A + B + S')}{(X + B + S)} \quad (Sc)$$

Elimination of S and S' among Eqs. Sa – Sc gives

$$\begin{aligned} X + B + \sqrt{(X + B)^2 + 4K_s} \\ = (A + B + \sqrt{(A + B)^2 + 4K_s})/10^{V/0.0591} \end{aligned} \quad (Sd)$$

Equation Sd may be solved explicitly for X .

$$X = \frac{A'}{10^{V/0.0591}} - \frac{10^{V/0.0591}}{A'} K_s - B \quad (Se)$$

where

$$A' = (A + B + \sqrt{(A + B)^2 + 4K_s})/2$$

Before X may be calculated from values of V and A as in Exp. 22.1' the constant parameters B and K_s must be evaluated for the particular reagents and working conditions that are selected. Measurement of a blank and a sample of known chloride concentration (different from the standard) gives two simultaneous equations of the type Se that may be solved for B and K_s . With B and K_s known in Eq. Se , X is calculable from values of V and A . Whenever working conditions change, B and K_s must be redetermined. With a little care, chloride concentrations down to $10^{-6}\ M$ may be determined.

SUPPLEMENTARY QUESTIONS AND PROBLEMS

S1. Under what conditions does Eq. Se reduce to Eq. 22.5?

S2. Suppose that a sample series ranges from 10^{-6} to $10^{-4}\ M$ chloride in the diluted solution. (a) Explain how you would choose the chloride concentration in the standard solution. (b) Explain how you would choose the chloride concentration in the known solution which, along with the blank, is used to determine B and K_s in Eq. Se .

S3. Explain how you would select conditions to permit extension of the lower limit to 10^{-7} *M* chloride.

S4. Solve Eq. *Sd* explicitly for *X*, to give Eq. *Se*.

S5. By the method described on page 642, show that for chloride concentrations above 10^{-4} *M*, the standard deviation (*x*) of *X* has the following dependence upon the standard deviation (*v*) of *V*.

$$\frac{x}{X} = \frac{v}{0.0591 \times 0.4343}$$

What relative standard deviation in *X* is caused by a standard deviation of 0.10 mv in *V*? *Ans.* 0.39%.

APPENDICES

IA. Table of Four-Place Logarithms

The *logarithm* (i.e., log) of a number is the power to which 10 must be raised to give the number. Thus

$$x = 10^{\log x}$$

The *antilog* of a logarithm is the number corresponding to the log. In the above equation, x is the antilog of $\log x$.

A log is an exponent. Since exponents are added in multiplication, it becomes a simple additive process when performed with logs. Similarly, division, raising to a power, and extracting roots are simplified. Such simplification is a principal reason for the use of logs in computations.

1. *To find the log of a number.* Rearrange the number to be a number between 1 and 10 multiplied by some power of 10. The log of the number factor may be found in the table (decimals omitted). The log of the exponential factor is the exponent itself. These are then added to give the log of the number.

Example 1. Find $\log 222$.

$$\log 222 = \log (2.22 \times 10^2) = \log 2.22 + \log 10^2 = 0.3464 + 2 = 2.3464$$

Example 2. Find $\log 0.0222$.

$$\log 0.0222 = \log (2.22 \times 10^{-2}) = \log 2.22 + \log 10^{-2} = 0.3464 - 2 = -1.6536$$

If the number contains more than three digits, it may be necessary to interpolate. After some practice, the column labeled "Proportional Parts" permits mental interpolation. The four-place log table cannot be used for numbers with more than four significant digits. For more precise calculations, a table with more places (Appendix IB) is required; alternatively, longhand or a machine calculator may be used. For computations involving numbers with only three significant digits, the slide rule may be used.

Example 3. Find $\log 3.236$.

$$\left. \begin{array}{l} \log 3.24 = 5105 \\ \log 3.23 = 5092 \end{array} \right\} \begin{array}{l} \log 3.236 \text{ is } 0.6 \text{ of} \\ \text{the way between} \\ \text{these two logs} \end{array}$$

13, difference

$$\log 3.236 = 5092 + 0.6(13), \text{ or } 5100$$

The interpolation process may be speeded by using data in the Proportional Parts columns. Thus 8 must be added to log 3.23 to give log 3.236.

2. *To find the antilog of a log.* Rearrange the log to be a positive decimal number plus or minus an integer. The antilog of the decimal part may be found from the table, and is a number between 1 and 10. The antilog of the integer is 10 raised to that power.

Example 4. Find antilog 2.4023.

$$\text{antilog } 2.4023 = \text{antilog } (0.4023 + 2) = 2.525 \times 10^2$$

Example 5. Find antilog -4.3075 .

The antilog of -0.3075 cannot be found in the table; therefore, -4.3075 should be expressed as $0.6925 - 5$ so that the table may be used.

$$\text{antilog } -4.3075 = \text{antilog } (0.6925 - 5) = 4.926 \times 10^{-5}$$

3. *Multiplication or division with logs.* In computing the value of

$$\frac{a \times b \times c \times \cdots}{m \times n \times p \times \cdots}$$

$$\text{Log Ans.} = (\log a + \log b + \log c + \cdots) - (\log m + \log n + \log p + \cdots)$$

Example 6. Using logs, find the value of

$$\frac{1.034 \times 1.024 \times 0.4876}{0.02027 \times 152.4 \times 192.8}$$

Rearrange to

$$\frac{1.034 \times 1.024 \times 4.876 \times (10^{-1})}{2.027 \times 1.524 \times 1.928 \times (10^2)}$$

$$\log 1.034 = 0.0145$$

$$\log 2.027 = 0.3069$$

$$\log 1.024 = 0.0103$$

$$\log 1.524 = 0.1829$$

$$\log 4.876 = 0.6880$$

$$\log 1.928 = 0.2851$$

$$\log \text{ num.} = 0.7128$$

$$\log \text{ denom.} = 0.7749$$

If the log of the denominator were subtracted from that of the numerator, the antilog of resulting negative number could not be found in the table. The following subterfuge is used.

$$\begin{array}{r} 1.7128 - 1 \text{ (log num.)} \\ -0.7749 \quad \text{(log denom.)} \\ \hline \end{array}$$

$$0.9379 - 1 \text{ (log num./denom.)}$$

$$\text{Ans.} = 8.668 \times 10^{-1} \times (10^{-3}) = 8.668 \times 10^{-4}$$

(The factor in parentheses is carried down from the original statement of the problem.)

4. *Powers and roots with logs.* In computing the power or root of a number,

$$\log a^n = n \log a$$

$$\log \sqrt[n]{a} = \frac{1}{n} (\log a)$$

Example 7. Find $(2.435 \times 10^4)^6$.

$$(2.435 \times 10^4)^6 = (2.435)^6 \times (10^{24})$$

$$\log (2.435)^6 = 6(\log 2.435) = 6 \times 0.3865 = 2.3190$$

Therefore,

$$(2.435)^6 = 2.084 \times 10^2$$

$$Ans. = 2.084 \times 10^2 \times (10^{24}) = 2.084 \times 10^{26}$$

To find a root, rearrange the number so that it contains a power of ten which is a multiple of the root, and another numerical factor which is greater than unity. The power of ten may then be rooted directly, without using logs, and only the number factor need be treated with logs. This is particularly useful with decimal numbers, since negative logarithms are avoided.

Example 8. Find $\sqrt[3]{0.0004572}$.

$$(0.0004572)^{1/3} = (457.2 \times 10^{-6})^{1/3} = (457.2)^{1/3} \times (10^{-2})$$

$$\log (457.2)^{1/3} = (1/3) \log (4.572 \times 10^2) = (1/3)(2.6601) = 0.8867$$

Therefore,

$$(457.2)^{1/3} = 7.704$$

$$Ans. = 7.704 \times 10^{-2}$$

IA. Table of Four-Place Logarithms

										Proportional Parts									
0 1 2 3 4					5 6 7 8 9														
										1	2	3	4	5	6	7	8	9	
10	0000	0043	0086	0128	0170	0212	0253	0294	0334	0374	4	8	12	17	21	25	29	33	37
11	0414	0453	0492	0531	0569	0607	0645	0682	0719	0755	4	8	11	15	19	23	26	30	34
12	0792	0828	0864	0899	0934	0969	1004	1038	1072	1106	3	7	10	14	17	21	24	28	31
13	1139	1173	1206	1239	1271	1303	1335	1367	1399	1430	3	6	10	13	16	19	23	26	29
14	1461	1492	1523	1553	1584	1614	1644	1673	1703	1732	3	6	9	12	15	18	21	24	27
15	1761	1790	1818	1847	1875	1903	1931	1959	1987	2014	3	6	8	11	14	17	20	22	25
16	2041	2068	2095	2122	2148	2175	2201	2227	2253	2279	3	5	8	11	13	16	18	21	24
17	2304	2330	2355	2380	2405	2430	2455	2480	2504	2529	2	5	7	10	12	15	17	20	22
18	2553	2577	2601	2625	2648	2672	2695	2718	2742	2765	2	5	7	9	12	14	16	19	21
19	2788	2810	2833	2856	2878	2900	2923	2945	2967	2989	2	4	7	9	11	13	16	18	20
20	3010	3032	3054	3075	3096	3118	3139	3160	3181	3201	2	4	6	8	11	13	15	17	19
21	3222	3243	3263	3284	3304	3324	3345	3365	3385	3404	2	4	6	8	10	12	14	16	18
22	3424	3444	3464	3483	3502	3522	3541	3560	3579	3598	2	4	6	8	10	12	14	15	17
23	3617	3636	3655	3674	3692	3711	3729	3747	3766	3784	2	4	6	7	9	11	13	15	17
24	3802	3820	3838	3856	3874	3892	3909	3927	3945	3962	2	4	5	7	9	11	12	14	16
25	3979	3997	4014	4031	4048	4065	4082	4099	4116	4133	2	3	5	7	9	10	12	14	15
26	4150	4166	4183	4200	4216	4232	4249	4265	4281	4298	2	3	5	7	8	10	11	13	15
27	4314	4330	4346	4362	4378	4393	4409	4425	4440	4456	2	3	5	6	8	9	11	13	14
28	4472	4487	4502	4518	4533	4548	4564	4579	4594	4609	2	3	5	6	8	9	11	12	14
29	4624	4639	4654	4669	4683	4698	4713	4728	4742	4757	1	3	4	6	7	9	10	12	13
30	4771	4786	4800	4814	4829	4843	4857	4871	4886	4900	1	3	4	6	7	9	10	11	13
31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
32	5051	5065	5079	5092	5105	5119	5132	5145	5159	5172	1	3	4	5	7	8	9	11	12
33	5185	5198	5211	5224	5237	5250	5263	5276	5289	5302	1	3	4	5	6	8	9	10	12
34	5315	5328	5340	5353	5366	5378	5391	5403	5416	5428	1	3	4	5	6	8	9	10	11
35	5441	5453	5465	5478	5490	5502	5514	5527	5539	5551	1	2	4	5	6	7	9	10	11
36	5563	5575	5587	5599	5611	5623	5635	5647	5658	5670	1	2	4	5	6	7	8	10	11
37	5682	5694	5705	5717	5729	5740	5752	5763	5775	5786	1	2	3	5	6	7	8	9	10
38	5798	5809	5821	5832	5843	5855	5866	5877	5888	5899	1	2	3	5	6	7	8	9	10
39	5911	5922	5933	5944	5955	5966	5977	5988	5999	6010	1	2	3	4	5	7	8	9	10
40	6021	6031	6042	6053	6064	6075	6085	6096	6107	6117	1	2	3	4	5	6	8	9	10
41	6128	6138	6149	6160	6170	6180	6191	6201	6212	6222	1	2	3	4	5	6	7	8	9
42	6232	6243	6253	6263	6274	6284	6294	6304	6314	6325	1	2	3	4	5	6	7	8	9
43	6335	6345	6355	6365	6375	6385	6395	6405	6415	6425	1	2	3	4	5	6	7	8	9
44	6435	6444	6454	6464	6474	6484	6493	6503	6513	6522	1	2	3	4	5	6	7	8	9
45	6532	6542	6551	6561	6571	6580	6590	6599	6609	6618	1	2	3	4	5	6	7	8	9
46	6628	6637	6646	6656	6665	6675	6684	6693	6702	6712	1	2	3	4	5	6	7	7	8
47	6721	6730	6739	6749	6758	6767	6776	6785	6794	6803	1	2	3	4	5	5	6	7	8
48	6812	6821	6830	6839	6848	6857	6866	6875	6884	6893	1	2	3	4	4	5	6	7	8
49	6902	6911	6920	6928	6937	6946	6955	6964	6972	6981	1	2	3	4	4	5	6	7	8
50	6990	6998	7007	7016	7024	7033	7042	7050	7059	7067	1	2	3	3	4	5	6	7	8
51	7076	7084	7093	7101	7110	7118	7126	7135	7143	7152	1	2	3	3	4	5	6	7	8
52	7160	7168	7177	7185	7193	7202	7210	7218	7226	7235	1	2	2	3	4	5	6	7	7
53	7243	7251	7259	7267	7275	7284	7292	7300	7308	7316	1	2	2	3	4	5	6	6	7
54	7324	7332	7340	7348	7356	7364	7372	7380	7388	7396	1	2	2	3	4	5	6	6	7

IA. Table of Four-Place Logarithms—Cont.

0 1 2 3 4					5 6 7 8 9					Proportional Parts									
										1	2	3	4	5	6	7	8	9	
55	7404	7412	7419	7427	7435	7443	7451	7459	7466	7474	1	2	2	3	4	5	5	6	7
56	7482	7490	7497	7505	7513	7520	7528	7536	7543	7551	1	2	2	3	4	5	5	6	7
57	7559	7566	7574	7582	7589	7597	7604	7612	7619	7627	1	2	2	3	4	5	5	6	7
58	7634	7642	7649	7657	7664	7672	7679	7686	7694	7701	1	1	2	3	4	4	5	6	7
59	7709	7716	7723	7731	7738	7745	7752	7760	7767	7774	1	1	2	3	4	4	5	6	7
60	7782	7789	7796	7803	7810	7818	7825	7832	7839	7846	1	1	2	3	4	4	5	6	6
61	7853	7860	7868	7875	7882	7889	7896	7903	7910	7917	1	1	2	3	4	4	5	6	6
62	7924	7931	7938	7945	7952	7959	7966	7973	7980	7987	1	1	2	3	3	4	5	6	6
63	7993	8000	8007	8014	8021	8028	8035	8041	8048	8055	1	1	2	3	3	4	5	5	6
64	8062	8069	8075	8082	8089	8096	8102	8109	8116	8122	1	1	2	3	3	4	5	5	6
65	8129	8136	8142	8149	8156	8162	8169	8176	8182	8189	1	1	2	3	3	4	5	5	6
66	8195	8202	8209	8215	8222	8228	8235	8241	8248	8254	1	1	2	3	3	4	5	5	6
67	8261	8267	8274	8280	8287	8293	8299	8306	8312	8319	1	1	2	3	3	4	5	5	6
68	8325	8331	8338	8344	8351	8357	8363	8370	8376	8382	1	1	2	3	3	4	4	5	6
69	8388	8395	8401	8407	8414	8420	8426	8432	8439	8445	1	1	2	2	3	4	4	5	6
70	8451	8457	8463	8470	8476	8482	8488	8494	8500	8506	1	1	2	2	3	4	4	5	6
71	8513	8519	8525	8531	8537	8543	8549	8555	8561	8567	1	1	2	2	3	4	4	5	5
72	8573	8579	8585	8591	8597	8603	8609	8615	8621	8627	1	1	2	2	3	4	4	5	5
73	8633	8639	8645	8651	8657	8663	8669	8675	8681	8686	1	1	2	2	3	4	4	5	5
74	8692	8698	8704	8710	8716	8722	8727	8733	8739	8745	1	1	2	2	3	4	4	5	5
75	8751	8756	8762	8768	8774	8779	8785	8791	8797	8802	1	1	2	2	3	3	4	5	5
76	8808	8814	8820	8825	8831	8837	8842	8848	8854	8859	1	1	2	2	3	3	4	5	5
77	8865	8871	8876	8882	8887	8893	8899	8904	8910	8915	1	1	2	2	3	3	4	4	5
78	8921	8927	8932	8938	8943	8949	8954	8960	8965	8971	1	1	2	2	3	3	4	4	5
79	8976	8982	8987	8993	8998	9004	9009	9015	9020	9026	1	1	2	2	3	3	4	4	5
80	9031	9036	9042	9047	9053	9058	9063	9069	9074	9079	1	1	2	2	3	3	4	4	5
81	9085	9090	9096	9101	9106	9112	9117	9122	9128	9133	1	1	2	2	3	3	4	4	5
82	9138	9143	9149	9154	9159	9165	9170	9175	9180	9186	1	1	2	2	3	3	4	4	5
83	9191	9196	9201	9206	9212	9217	9222	9227	9232	9238	1	1	2	2	3	3	4	4	5
84	9243	9248	9253	9258	9263	9269	9274	9279	9284	9289	1	1	2	2	3	3	4	4	5
85	9294	9299	9304	9309	9315	9320	9325	9330	9335	9340	1	1	2	2	3	3	4	4	5
86	9345	9350	9355	9360	9365	9370	9375	9380	9385	9390	1	1	2	2	3	3	4	4	5
87	9395	9400	9405	9410	9415	9420	9425	9430	9435	9440	0	1	1	2	2	3	3	4	4
88	9445	9450	9455	9460	9465	9469	9474	9479	9484	9489	0	1	1	2	2	3	3	4	4
89	9494	9499	9504	9509	9513	9518	9523	9528	9533	9538	0	1	1	2	2	3	3	4	4
90	9542	9547	9552	9557	9562	9566	9571	9576	9581	9586	0	1	1	2	2	3	3	4	4
91	9590	9595	9600	9605	9609	9614	9619	9624	9628	9633	0	1	1	2	2	3	3	4	4
92	9638	9643	9647	9652	9657	9661	9666	9671	9675	9680	0	1	1	2	2	3	3	4	4
93	9685	9689	9694	9699	9703	9708	9713	9717	9722	9727	0	1	1	2	2	3	3	4	4
94	9731	9736	9741	9745	9750	9754	9759	9763	9768	9773	0	1	1	2	2	3	3	4	4
95	9777	9782	9786	9791	9795	9800	9805	9809	9814	9818	0	1	1	2	2	3	3	4	4
96	9823	9827	9832	9836	9841	9845	9850	9854	9859	9863	0	1	1	2	2	3	3	4	4
97	9868	9872	9877	9881	9886	9890	9894	9899	9903	9908	0	1	1	2	2	3	3	4	4
98	9912	9917	9921	9926	9930	9934	9939	9943	9948	9952	0	1	1	2	2	3	3	4	4
99	9956	9961	9965	9969	9974	9978	9983	9987	9991	9996	0	1	1	2	2	3	3	3	4

IB. Table of Five-Place Logarithms (10000-20000) †

	0	1	2	3	4	5	6	7	8	9	Proportional Parts
100	00 000	043	087	130	173	217	260	303	346	389	
101	432	475	518	561	604	647	689	732	775	817	44 43 42
102	860	903	945	988	*030	*072	*115	*157	*199	*242	1 4 4 4
103	01 284	326	368	410	452	494	536	578	620	662	2 9 9 8
104	703	745	787	828	870	912	953	995	*036	*078	3 13 13 13
											4 18 17 17
105	02 119	160	202	243	284	325	366	407	449	490	5 22 22 21
106	531	572	612	653	694	735	776	816	857	898	6 26 26 25
107	938	979	*019	*060	*100	*141	*181	*222	*262	*302	7 31 30 29
108	03 342	383	423	463	503	543	583	623	663	703	8 35 34 34
109	743	782	822	862	902	941	981	*021	*060	*100	9 40 39 38
110	04 139	179	218	258	297	336	376	415	454	493	
111	532	571	610	650	689	727	766	805	844	883	41 40 39
112	922	961	999	*038	*077	*115	*154	*192	*231	*269	1 4 4 4
113	05 308	346	385	423	461	500	538	576	614	652	2 8 8 8
114	690	729	767	805	843	881	918	956	994	*032	3 12 12 12
											4 16 16 16
115	06 070	108	145	183	221	258	296	333	371	408	5 21 20 20
116	446	483	521	558	595	633	670	707	744	781	6 25 24 23
117	819	856	893	930	967	*004	*041	*078	*115	*151	7 29 28 27
118	07 188	225	262	298	335	372	408	445	482	518	8 33 32 31
119	555	591	628	664	700	737	773	809	846	882	9 37 36 35
120	918	954	990	*027	*063	*099	*135	*171	*207	*243	
121	08 279	314	350	386	422	458	493	529	565	600	38 37 36
122	636	672	707	743	778	814	849	884	920	955	1 4 4 4
123	991	*026	*061	*096	*132	*167	*202	*237	*272	*307	2 8 7 7
124	09 342	377	412	447	482	517	552	587	621	656	3 11 11 11
											4 15 15 14
125	691	726	760	795	830	864	899	934	968	*003	5 19 19 18
126	10 037	072	106	140	175	209	243	278	312	346	6 23 22 22
127	380	415	449	483	517	551	585	619	653	687	7 27 26 25
128	721	755	789	823	857	890	924	958	992	*025	8 30 30 29
129	11 059	093	126	160	193	227	261	294	327	361	9 34 33 32
130	394	428	461	494	528	561	594	628	661	694	
131	727	760	793	826	860	893	926	959	992	*024	35 34 33
132	12 057	090	123	156	189	222	254	287	320	352	1 4 3 3
133	385	418	450	483	516	548	581	613	646	678	2 7 7 7
134	710	743	775	808	840	872	905	937	969	*001	3 11 10 10
											4 14 14 13
135	13 033	066	098	130	162	194	226	258	290	322	5 18 17 17
136	354	386	418	450	481	513	545	577	609	640	6 21 20 20
137	672	704	735	767	799	830	862	893	925	956	7 25 24 23
138	988	*019	*051	*082	*114	*145	*176	*208	*239	*270	8 28 27 26
139	14 301	333	364	395	426	457	489	520	551	582	9 32 31 30
140	613	644	675	706	737	768	799	829	860	891	
141	922	953	983	*014	*045	*076	*106	*137	*168	*198	32 31 30
142	15 229	259	290	320	351	381	412	442	473	503	1 3 3 3
143	534	564	594	625	655	685	715	746	776	806	2 6 6 6
144	836	866	897	927	957	987	*017	*047	*077	*107	3 10 9 9
											4 13 12 12
145	16 137	167	197	227	256	286	316	346	376	406	5 16 16 15
146	435	465	495	524	554	584	613	643	673	702	6 19 19 18
147	732	761	791	820	850	879	909	938	967	997	7 22 22 21
148	17 026	056	085	114	143	173	202	231	260	289	8 26 25 24
149	319	348	377	406	435	464	493	522	551	580	9 29 28 27

† Four-place tables are relatively less precise for low numbers (1000-2000) than for high numbers (9000-10000). The above five-place table may be a useful adjunct to the four-place table of Appendix IA.

IB. Table of Five-Place Logarithms—Cont.

	0	1	2	3	4	5	6	7	8	9	Proportional Parts	
150	17 609	638	667	696	725	754	782	811	840	869		
151	898	926	955	984	*013	*041	*070	*099	*127	*156	29	28
152	18 184	213	241	270	298	327	355	384	412	441	1	2.9 2.8
153	469	498	526	554	583	611	639	667	696	724	2	5.8 5.6
154	752	780	808	837	865	893	921	949	977	*005	3	8.7 8.4
											4	11.6 11.2
155	19 033	061	089	117	145	173	201	229	257	285	5	14.5 14.0
156	312	340	368	396	424	451	479	507	535	562	6	17.4 16.8
157	590	618	645	673	700	728	756	783	811	838	7	20.3 19.6
158	866	893	921	948	976	*003	*030	*058	*085	*112	8	23.2 22.4
159	20 140	167	194	222	249	276	303	330	358	385	9	26.1 25.2
160	412	439	466	493	520	548	575	602	629	656		
161	683	710	737	763	790	817	844	871	898	925	27	26
162	952	978	*005	*032	*059	*085	*112	*139	*165	*192	1	2.7 2.6
163	21 219	245	272	299	325	352	378	405	431	458	2	5.4 5.2
164	484	511	537	564	590	617	643	669	696	722	3	8.1 7.8
											4	10.8 10.4
165	748	775	801	827	854	880	906	932	958	985	5	13.5 13.0
166	22 011	037	063	089	115	141	167	194	220	246	6	16.2 15.6
167	272	298	324	350	376	401	427	453	479	505	7	18.9 18.2
168	531	557	583	608	634	660	686	712	737	763	8	21.6 20.8
169	789	814	840	866	891	917	943	968	994	*019	9	24.3 23.4
170	23 045	070	096	121	147	172	198	223	249	274		
171	300	325	350	376	401	426	452	477	502	528	25	
172	553	578	603	629	654	679	704	729	754	779	1	2.5
173	805	830	855	880	905	930	955	980	*005	*030	2	5.0
174	24 055	080	105	130	155	180	204	229	254	279	3	7.5
											4	10.0
175	304	329	353	378	403	428	452	477	502	527	5	12.5
176	551	576	601	625	650	674	699	724	748	773	6	15.0
177	797	822	846	871	895	920	944	969	993	*018	7	17.5
178	25 042	066	091	115	139	164	188	212	237	261	8	20.0
179	285	310	334	358	382	406	431	455	479	503	9	22.5
180	527	551	575	600	624	648	672	696	720	744		
181	768	792	816	840	864	888	912	935	959	983	24	23
182	26 007	031	055	079	102	126	150	174	198	221	1	2.4 2.3
183	245	269	293	316	340	364	387	411	435	458	2	4.8 4.6
184	482	505	529	553	576	600	623	647	670	694	3	7.2 6.9
											4	9.6 9.2
185	717	741	764	788	811	834	858	881	905	928	5	12.0 11.5
186	951	975	998	*021	*045	*068	*091	*114	*138	*161	6	14.4 13.8
187	27 184	207	231	254	277	300	323	346	370	393	7	16.8 16.1
188	416	439	462	485	508	531	554	577	600	623	8	19.2 18.4
189	646	669	692	715	738	761	784	807	830	852	9	21.6 20.7
190	875	898	921	944	967	989	*012	*035	*058	*081		
191	28 103	126	149	171	194	217	240	262	285	307	22	21
192	330	353	375	398	421	443	466	488	511	533	1	2.2 2.1
193	556	578	601	623	646	668	691	713	735	758	2	4.4 4.2
194	780	803	825	847	870	892	914	937	959	981	3	6.6 6.3
											4	8.8 8.4
195	29 003	026	048	070	092	115	137	159	181	203	5	11.0 10.5
196	226	248	270	292	314	336	358	380	403	425	6	13.2 12.6
197	447	469	491	513	535	557	579	601	623	645	7	15.4 14.7
198	667	688	710	732	754	776	798	820	842	863	8	17.6 16.8
199	885	907	929	951	973	994	*016	*038	*060	*081	9	19.8 18.9
200	30 103	125	146	168	190	211	233	255	276	298		

IIA. Table of Ordinates of the Normal Curve *

This table gives the height of an ordinate at a distance $|X - \mu|/\sigma$ from the mean, expressed as a decimal fraction of the height of the maximum ordinate.

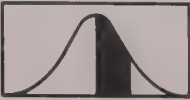
$\frac{X - \mu}{\sigma}$.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
0.0	1.00000	.99995	.99980	.99955	.99920	.99875	.99820	.99755	.99685	.99596
0.1	.99501	.99396	.99283	.99158	.99025	.98881	.98728	.98565	.98393	.98211
0.2	.98020	.97819	.97609	.97390	.97161	.96923	.96676	.96420	.96156	.95882
0.3	.95600	.95309	.95010	.94702	.94387	.94055	.93723	.93382	.93024	.92677
0.4	.92312	.91939	.91558	.91169	.90774	.90371	.89961	.89543	.89119	.88688
0.5	.88250	.87805	.87353	.86896	.86432	.85962	.85488	.85006	.84519	.84060
0.6	.83527	.83023	.82514	.82010	.81481	.80957	.80429	.79896	.79359	.78817
0.7	.78270	.77721	.77167	.76610	.76048	.75484	.74916	.74342	.73769	.73193
0.8	.72615	.72033	.71448	.70861	.70272	.69681	.69087	.68493	.67896	.67298
0.9	.66689	.66097	.65494	.64891	.64287	.63683	.63077	.62472	.61865	.61259
1.0	.60653	.60047	.59440	.58834	.58228	.57623	.57017	.56414	.55810	.55209
1.1	.54607	.54007	.53409	.52812	.52214	.51620	.51027	.50437	.49848	.49260
1.2	.48675	.48092	.47511	.46933	.46357	.45783	.45212	.44644	.44078	.43516
1.3	.42956	.42399	.41845	.41294	.40747	.40202	.39661	.39123	.38559	.38058
1.4	.37531	.37007	.36487	.35971	.35459	.34950	.34445	.33944	.33447	.32954
1.5	.32465	.31980	.31500	.31023	.30550	.30082	.29618	.29158	.28702	.28251
1.6	.27804	.27361	.26923	.26489	.26059	.25634	.25213	.24797	.24385	.23978
1.7	.23575	.23176	.22782	.22392	.22008	.21627	.21251	.20879	.20511	.20148
1.8	.19790	.19436	.19086	.18741	.18400	.18064	.17732	.17404	.17081	.16762
1.9	.16448	.16137	.15831	.15530	.15232	.14939	.14650	.14364	.14083	.13806
2.0	.13534	.13265	.13000	.12740	.12483	.12230	.11981	.11737	.11496	.11259
2.1	.11025	.10795	.10570	.10347	.10129	.09914	.09702	.09495	.09290	.09090
2.2	.08892	.08698	.08507	.08320	.08136	.07956	.07778	.07604	.07433	.07265
2.3	.07100	.06939	.06780	.06624	.06471	.06321	.06174	.06029	.05888	.05750
2.4	.05614	.05481	.05350	.05222	.05096	.04973	.04852	.04734	.04618	.04505
2.5	.04394	.04285	.04179	.04074	.03972	.03873	.03775	.03680	.03586	.03494
2.6	.03405	.03317	.03232	.03148	.03066	.02986	.02908	.02831	.02757	.02684
2.7	.02612	.02542	.02474	.02408	.02343	.02280	.02218	.02157	.02098	.02040
2.8	.01984	.01929	.01876	.01823	.01772	.01723	.01674	.01627	.01581	.01536
2.9	.01492	.01449	.01408	.01367	.01328	.01288	.01252	.01215	.01179	.01145
3.0	.01111	.01078	.01046	.01015	.00984	.00955	.00926	.00898	.00871	.00845
3.1	.00819	.00794	.00769	.00746	.00723	.00700	.00679	.00658	.00637	.00617
3.2	.00598	.00579	.00560	.00543	.00525	.00509	.00492	.00477	.00461	.00446
3.3	.00432	.00418	.00404	.00391	.00378	.00366	.00354	.00342	.00331	.00320
3.4	.00309	.00299	.00289	.00279	.00269	.00260	.00251	.00243	.00235	.00227
3.5	.00219	.00211	.00204	.00197	.00190	.00183	.00177	.00171	.00165	.00159
3.6	.00153	.00148	.00143	.00138	.00133	.00128	.00123	.00119	.00115	.00110
3.7	.00106	.00103	.00099	.00095	.00092	.00088	.00085	.00082	.00079	.00076
3.8	.00073	.00070	.00068	.00065	.00063	.00060	.00058	.00056	.00054	.00052
3.9	.00050	.00048	.00046	.00044	.00043	.00041	.00039	.00038	.00036	.00035
4.0	.00034									
4.5	.00004									
5.0	.00000									

* Reprinted from F. E. Croxton and D. J. Cowden, *Practical Business Statistics*, 2d ed. (Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1948), p. 509, by permission of the publisher.

IIB. Table of Areas under the Normal Curve *

From the mean to distances $X - \mu / \sigma$ from the mean, expressed as decimal fractions of the total area, 1.0000.

This table shows:



$\frac{X - \mu}{\sigma}$.00	.01	.02	.03	.04	.05	.06	.07	.08	.09
0.0	.00000	.00399	.00798	.01197	.01595	.01994	.02392	.02790	.03188	.03586
0.1	.03983	.04380	.04776	.05172	.05567	.05962	.06356	.06749	.07142	.07535
0.2	.07926	.08317	.08706	.09095	.09483	.09871	.10257	.10642	.11026	.11409
0.3	.11791	.12172	.12552	.12930	.13307	.13683	.14058	.14431	.14803	.15173
0.4	.15542	.15910	.16276	.16640	.17003	.17364	.17724	.18082	.18439	.18793
0.5	.19146	.19497	.19847	.20194	.20540	.20884	.21226	.21566	.21904	.22240
0.6	.22575	.22907	.23237	.23565	.23891	.24215	.24537	.24857	.25175	.25490
0.7	.25804	.26115	.26424	.26730	.27035	.27337	.27637	.27935	.28230	.28524
0.8	.28814	.29103	.29389	.29673	.29955	.30234	.30511	.30785	.31057	.31327
0.9	.31594	.31859	.32121	.32381	.32639	.32894	.33147	.33398	.33646	.33891
1.0	.34134	.34375	.34614	.34850	.35083	.35314	.35543	.35769	.35993	.36214
1.1	.36433	.36650	.36864	.37076	.37286	.37493	.37698	.37900	.38100	.38298
1.2	.38493	.38686	.38877	.39065	.39251	.39435	.39617	.39796	.39973	.40147
1.3	.40320	.40490	.40658	.40824	.40988	.41149	.41309	.41466	.41621	.41774
1.4	.41924	.42073	.42220	.42364	.42507	.42647	.42786	.42922	.43056	.43189
1.5	.43319	.43448	.43574	.43699	.43822	.43943	.44062	.44179	.44295	.44408
1.6	.44520	.44630	.44738	.44845	.44950	.45053	.45154	.45254	.45352	.45449
1.7	.45543	.45637	.45728	.45818	.45907	.45994	.46080	.46164	.46246	.46327
1.8	.46407	.46485	.46562	.46638	.46712	.46784	.46856	.46926	.46995	.47062
1.9	.47128	.47193	.47257	.47320	.47381	.47441	.47500	.47558	.47615	.47670
2.0	.47725	.47778	.47831	.47882	.47932	.47982	.48030	.48077	.48124	.48169
2.1	.48214	.48257	.48300	.48341	.48382	.48422	.48461	.48500	.48537	.48574
2.2	.48610	.48645	.48679	.48713	.48745	.48778	.48809	.48840	.48870	.48899
2.3	.48928	.48956	.48983	.49010	.49036	.49061	.49086	.49111	.49134	.49158
2.4	.49180	.49202	.49224	.49245	.49266	.49286	.49305	.49324	.49343	.49361
2.5	.49379	.49396	.49413	.49430	.49446	.49461	.49477	.49492	.49506	.49520
2.6	.49534	.49547	.49560	.49573	.49585	.49598	.49609	.49621	.49632	.49643
2.7	.49653	.49664	.49674	.49683	.49693	.49702	.49711	.49720	.49728	.49736
2.8	.49744	.49752	.49760	.49767	.49774	.49781	.49788	.49795	.49801	.49807
2.9	.49813	.49819	.49825	.49831	.49836	.49841	.49846	.49851	.49856	.49861
3.0	.49865	.49869	.49874	.49878	.49882	.49886	.49889	.49893	.49897	.49900
3.1	.49903	.49906	.49910	.49913	.49916	.49918	.49921	.49924	.49926	.49929
3.2	.49931	.49934	.49936	.49938	.49940	.49942	.49944	.49946	.49948	.49950
3.3	.49952	.49953	.49955	.49957	.49958	.49960	.49961	.49962	.49964	.49965
3.4	.49966	.49968	.49969	.49970	.49971	.49972	.49973	.49974	.49975	.49976
3.5	.49977	.49978	.49978	.49979	.49980	.49981	.49982	.49982	.49983	.49984
3.6	.49984	.49985	.49985	.49986	.49986	.49987	.49987	.49988	.49988	.49989
3.7	.49989	.49990	.49990	.49990	.49991	.49991	.49992	.49992	.49992	.49992
3.8	.49993	.49993	.49993	.49994	.49994	.49994	.49994	.49995	.49995	.49995
3.9	.49995	.49995	.49996	.49996	.49996	.49996	.49996	.49996	.49997	.49997
4.0	.4999683									
4.5	.4999966									
5.0	.4999997134									

* Reprinted in part from F. E. Croxton and D. J. Cowden, *Practical Business Statistics*, 2d ed. (Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1948), p. 511, by permission of the publisher.

III. Individual Locker Equipment for Experiments in This Book*

Volumetric equipment (graduated glassware)

- 2 Burets, 50-ml, with glass or Teflon stopcocks
- 3 Cylinders, graduated, 10-ml, 25-ml, 100-ml
- 2 Flasks, glass-stoppered volumetric, 250-ml, 500-ml
- 2 Pipets, volumetric, 25-ml, 50-ml
- 1 Pipet, graduated, 10-ml

Miscellaneous glassware

- 9 Beakers
 - 1 150-ml 1 600-ml
 - 3 250-ml 1 800-ml
 - 3 400-ml
- 12 Bottles
 - 2 250-ml glass-stoppered reagent
 - 2 500-ml glass-stoppered reagent
 - 2 1-l glass-stoppered reagent
 - 1 1-l plastic reagent
 - 1 100-ml plastic wash
 - 2 weighing, small
 - 1 250-ml wide-mouthed, with 2-hole rubber stopper
 - 1 500-ml wide-mouthed, glass-stoppered
- 1 Desiccator, with porcelain plate and wire gauze
- 9 Flasks, Erlenmeyer
 - 2 125-ml
 - 4 250-ml
 - 3 500-ml
- 3 Flasks, Florence
 - 1 500-ml
 - 2 1-l
- 1 Flask, 1-l filter, with 2-hole rubber stopper and suction hose
- 4 Funnels
 - 3 long-stemmed, $2\frac{1}{2}$ -inch diameter, 60°
 - 1 short-stemmed, $2\frac{1}{2}$ -inch diameter, 60°
- 1 T-joint, for safety bottle

- 1 Thermometer, -10 to 110°C
- 12 Watch glasses, 3 each, of 2", $3\frac{1}{2}$ ", 4", and $4\frac{1}{2}$ " diameters

Miscellaneous equipment

- 1 Apron, or laboratory coat
- 3 Burners, Bunsen, with rubber tubing
- 5 Clamps
 - 1 test-tube
 - 2 pinch
 - 2 screw
- 1 File, triangular
- 1 Forceps, cadmium or nickel plated
- 1 Lock and key
- Porcelain ware
 - 3 crucibles, No. 00, with covers
 - 3 crucibles, Gooch, with Witte plates†
- Rubber goods
 - Bulbs: 3 5-ml
 - 1 50-ml
- Gooch rubber
- Stoppers: 2 2-hole, to fit wash bottles
- 3 solid, to fit 250-ml Erlenmeyer flasks
- 2 solid, to fit 125-ml Erlenmeyer flasks
- 1 Spatula, 3-inch stainless steel
- 1 Tongs, for crucibles
- 3 Triangles, Nichrome
- 1 Weight set, with forceps and quill brush, in plastic bag
- 3 Wire screens, 4 inches by 4 inches
- 1 Wing top, for burner

Expendable equipment

- Matches
- Towelling (cheesecloth)
- Filter paper
 - ashless, fine
 - qualitative, coarse
- Cellulose sponge

* Ringstands and associated iron ware may be set up conveniently on a community basis, and so may bottle, test tube, and buret brushes.

† Or 3 sintered glass filter crucibles, medium porosity.

IVA. Chemical Reagents

Reagent*	Formula	Molecular Weight	Density, 25°C, g/cc	Solubility, 25°C, g/100 g H ₂ O
Alcohol, 95% (ethyl)	C ₂ H ₅ OH	46.07	0.804	miscible
Ammonium bifluoride	NH ₄ HF ₂	57.05	1.21 (12°)	very soluble
Ammonium chloride	NH ₄ Cl	53.50	1.53 (17°)	29.4 (0°)
Ammonium oxalate	(NH ₄) ₂ C ₂ O ₄ · H ₂ O	142.12	1.50	5.0†
Ammonium persulfate	(NH ₄) ₂ S ₂ O ₈	228.21	1.98	58.2 (0°)
† Ammonium sulfate	(NH ₄) ₂ SO ₄	132.15	1.77 (20°)	77
† Barium chloride	BaCl ₂ · 2H ₂ O	244.31	3.10 (24°)	36.9§
Barium diphenylamine sulfonate of tetrabromo-m-cresolsulfon-phthalein)	(C ₁₂ H ₁₀ O ₃ NS) ₂ Ba	633.91		slightly soluble
Benzene, technical, for cleaning glassware	C ₆ H ₆	78.11	0.879 (20°)	0.07 (22°)
Bismuth nitrate	Bi(NO ₃) ₃ · 5H ₂ O	485.10	2.82	42 (19°)
Boric acid	H ₃ BO ₃	61.84	1.44 (15°)	6.0
Bromocresol green (sodium salt of tetrabromo-m-cresolsulfon-phthalein)	(C ₂₁ H ₁₂ O ₅ SBBr ₄)Na ₂	742.03		soluble
Bromine	Br ₂	159.83	3.119 (20°)	3.17
Calcium chloride, anhydrous, granular	CaCl ₂	110.99	2.15	59.5 (0°)
Calcium chloride, technical, anhydrous, 4-12 mesh, for desiccators				very soluble
Calcon	C ₂₀ H ₁₃ O ₅ N ₂ SSNa	416.40		
Ceric hydroxide	Ce(OH) ₄	208.15		insoluble
† Copper, foil, and 20-ga. wire	Cu	63.54	8.92 (20°)	insoluble
Cupric nitrate, crystalline	Cu(NO ₃) ₂ · 3H ₂ O	241.60	2.05 (4°)	381 (40°)
Dextrin	(C ₆ H ₁₀ O ₅) _x		1.04	slightly soluble
Dichlorofluorescein	C ₂₀ H ₁₀ O ₅ Cl ₂	401.20		slightly soluble
EDTA, disodium salt	C ₁₀ H ₁₄ N ₂ O ₈ Na ₂ · 2H ₂ O	372.24		
Eriochrome Black T	C ₂₀ H ₁₂ O ₇ N ₃ SSNa	461.39		
Ferric nitrate	Fe(NO ₃) ₃ · 9H ₂ O	404.02		very soluble
Glycerin, technical, for lubricant	C ₃ H ₈ O ₃	92.09	1.26 (20°)	miscible
† Iron wire, assayed	Fe	55.85	7.8	insoluble
Magnesium chloride, crystal	MgCl ₂ · 6H ₂ O	203.33	1.56	281 (0°)
Mercuric chloride	HgCl ₂	271.52	5.44	6.6§
Mercuric iodide	HgI ₂	454.43	6.28	0.006
Methyl orange	(CH ₃) ₂ N · C ₆ H ₄ · N · N · C ₆ H ₄ · SO ₃ Na	327.35		0.2
Nitrobenzene	C ₆ H ₅ · NO ₂	123.11	1.20 (18°)	0.2
† Oxalic acid	H ₂ C ₂ O ₄ · 2H ₂ O	126.07	1.65 (19°)	10 (20°)§
Phenolphthalein	C ₂₀ H ₁₄ O ₄	318.33	1.30	0.2 (20°)
Potassium				
† acid phthalate	KHC ₈ H ₄ O ₄	204.23	1.63	10.2
† chloride	KCl	74.56	1.99	35.5
chromate	K ₂ CrO ₄	194.21	2.73 (18°)	58.0 (0°)
† dichromate	K ₂ Cr ₂ O ₇	294.22	2.69	10.97 (20°)†
iodide	KI	166.01	3.13	148
periodate	KIO ₄	230.01	3.62	0.66 (13°)
permanganate	KMnO ₄	158.04	2.70	7.6
† sulfate	K ₂ SO ₄	174.23	2.66	10.7†
† thiocyanate	KSCN	97.18	1.89	217 (20°)
Silver wire, 20 ga., for Ag-AgCl electrodes	Ag	107.870	10.5	insoluble

* All chemicals should be analyzed reagent grade, unless otherwise specified.

† Chemicals that may also be used as primary or assayed standards, either in analysis or in preparation of unknown samples.

‡ Grams of anhydrous substance per 100 g of solution at indicated temperature.

§ Grams of anhydrous substance per 100 g of water at indicated temperature.

IVA. Chemical Reagents—Cont.

Reagent*	Formula	Molecular Weight	Density, 25°C, g/cc	Solubility, 25°C, g/100 g H ₂ O
† Silver nitrate	AgNO ₃	169.88	4.35 (19°)	72‡
Sodium acetate, granular	NaC ₂ H ₃ O ₂ ·3H ₂ O	136.09	1.45	46.5 (20°)§
bicarbonate	NaHCO ₃	84.01	2.20	10.3
† carbonate, anhydrous	Na ₂ CO ₃	105.99	2.53	25
† chloride	NaCl	58.45	2.16	35.9
cyanide, granular	NaCN	49.01		48 (10°)
dichromate, technical (for cleaning solution)	Na ₂ Cr ₂ O ₇ ·2H ₂ O	298.03	2.52 (13°)	178 (20°)§
hydroxide, pellets	NaOH	40.00	2.13	114
† oxalate	Na ₂ C ₂ O ₄	134.00	2.27	3.5‡
phosphate, technical (for cleaning)	Na ₃ PO ₄ ·12H ₂ O	380.15	1.62	15§
† sulfate	Na ₂ SO ₄	142.05		19.4 (20°)
† thiosulfate	Na ₂ S ₂ O ₃ ·5H ₂ O	248.19	1.68	70.1 (20°)§
Stannous chloride	SnCl ₂ ·2H ₂ O	225.65	2.71 (16°)	119 (0°)
Starch, soluble, powdered	(C ₆ H ₁₀ O ₅) _x			
† Sulfamic acid	NH ₂ ·SO ₃ H	97.10	2.03 (12°)	20 (0°)
Thymol	(CH ₃)(C ₃ H ₇)C ₆ H ₃ ·OH	150.22	0.972	0.09 (19°)
Urea	NH ₂ ·CO·NH ₂	60.06	1.335 (20°)	100 (17°)
Xylenol orange	C ₃₁ H ₃₂ O ₁₃ N ₂ S	672.67		

IVB. Solutions of Acids, Bases, and Salts

Reagent	Molecular Weight	Molarity	Weight Per Cent Reagent	Density (20°) (g/cc)	Preparation*
ACIDS					
Acetic	60.05	17.4	99.5	1.051	Reagent-grade glacial acid
Boric	61.84	0.65	4		Dissolve 40 g boric acid in 1 l water
Hydrochloric	36.46	12.4	38.0	1.188	Reagent-grade conc. HCl
Hydrofluoric	20.01	25.7	45.0	1.143	Reagent-grade conc. HF
Nitric	63.02	15.4	69.0	1.409	Reagent-grade conc. HNO ₃
Perchloric	100.47	11.6	70.0	1.668	Reagent-grade conc. HClO ₄
Phosphoric	98.00	14.7	85.0	1.689	Reagent-grade conc. H ₃ PO ₄
Sulfuric	98.08	17.6	94.0	1.831	Reagent-grade conc. H ₂ SO ₄
BASES					
Ammonia	17.032	14.8	28.0	0.898	Reagent-grade conc. NH ₃
Sodium hydroxide (50%)	40.00	19.1	50	1.525	†
Sodium hydroxide (6 M)	40.00	6.0	19.7	1.216	Dissolve 240 g NaOH, and make up to 1 l
SALTS					
AgNO ₃	169.89	0.5	7.96	1.068	Dissolve 85 g AgNO ₃ , and make up to 1 l
BaCl ₂	208.27	0.5	9.57	1.088	Dissolve 122 g BaCl ₂ ·2H ₂ O, and make up to 1 l
Cu(NO ₃) ₂	187.56	0.5	8.7	1.076	Dissolve 121 g Cu(NO ₃) ₂ ·3H ₂ O, and make up to 1 l
Fe(NO ₃) ₃	241.87	0.33	7.60	1.059	Dissolve 135 g Fe(NO ₃) ₃ ·9H ₂ O, and make up to 1 l
HgCl ₂	271.52	0.192	5.00	1.041	Dissolve 50 g HgCl ₂ in 950 ml water
KCl	74.56	3.80	24.3	1.165	Dissolve 284 g KCl, and make up to 1 l ‡
K ₂ CrO ₄	194.21	0.1	1.89	1.015	Dissolve 19.4 g K ₂ CrO ₄ , and make up to 1 l
NaC ₂ H ₃ O ₂	82.04	0.5	3.97	1.019	Dissolve 68 g NaC ₂ H ₃ O ₂ ·3H ₂ O, and make up to 1 l
Urea	60.06		4.0		Dissolve 40 g urea, and make up to 1 l

* Use distilled water in preparing all solutions.

† Stir 1550 g reagent-grade NaOH with 1500 ml water in a 3-l stainless steel beaker. Cover with watch glass until cool, and then decant into 1-l plastic bottles with tightly fitting caps for storage. Allow to settle at least 1 month. To withdraw solution, replace the cap with a cap equipped with a Kel-F or Teflon siphon, so that solution may be withdrawn without disturbing the settled precipitate, which is Na₂CO₃. The solution stored and dispensed in this way contains 0.2–0.4 mole per cent of Na₂CO₃, even after months of storage.

‡ This solution is almost saturated, and is used to refill saturated calomel electrodes as follows. Pour about 10 ml of the solution into a small beaker containing 2–3 g granulated KCl. Swirl for 1–2 minutes. Then, with a wide-orifice dropper, transfer some of the solution (along with some KCl crystals) to the electrode.

IVC. Indicator Solutions

Bromocresol green. Dissolve 1.0 g of sodium salt of bromocresol green in 1 l water.

Calcon. Dissolve 0.1 g in 10 ml of methanol. Filter through coarse paper and store in a dropper-top bottle for dispensing. Check every three weeks for deterioration by adding 2 drops to 100 ml of distilled water containing 10 drops of 50% NaOH and 0.1 g of NaCN. (CAUTION! Note 12, p. 592.) Less than a half-drop of 0.02 M CaCl_2 should be required to give a sharp transition from blue to pink.

Dichlorofluorescein. Dissolve 1.0 g of dichlorofluorescein in 700 ml ethyl alcohol and add 300 ml water.

Erio T. Dissolve 0.1 g in 10 ml of methanol. Filter through coarse paper and store in a dropper-top bottle for dispensing. Check every three weeks by adding 2 drops to 100 ml of distilled water containing 1 ml of pH 10 buffer and 0.1 g NaCN. (CAUTION! Note 12, p. 592.) Less than a half-drop of 0.02 M MgCl_2 should cause a sharp transition from blue to red-purple.

Ferroin. Use the 0.01 M ferroin solution distributed by the G. F. Smith Chemical Co., Columbus, Ohio.

Methyl orange. Dissolve 1.0 g in 1 l water.

Methyl red-bromocresol green. Dissolve 0.50 g of the sodium salt of methyl red and 0.75 g of the sodium salt of bromocresol green in 1 l of water.

Phenolphthalein. Dissolve 1.0 g in 1 l ethyl alcohol.

Sodium diphenylamine sulfonate. Dissolve 0.32 g of the barium salt in 100 ml water. Add 0.50 g Na_2SO_4 and filter to remove BaSO_4 .

Starch. Mix 1.0 g soluble starch and 0.010 g HgI_2 into a thin paste with water, and add slowly to 200 ml boiling water. Boil 5 minutes. Allow to cool and settle overnight, and then decant the clear supernatant liquid.

Xylenol orange. Dissolve 0.1 g in 10 ml of methanol. Filter through coarse paper and store in a dropper-top bottle for dispensing. Check every three weeks by adding 4 drops to 100 ml of 0.5 M HNO_3 . Less than a half-drop of 0.02 M $\text{Bi}(\text{NO}_3)_3$ should cause a sharp transition from yellow to red.

IVD. Miscellaneous Solutions

Asbestos suspension (for Gooch crucibles). The asbestos used for filtering must be of a good grade, so that it will not be affected appreciably by acid or dilute alkaline solutions. An acid-washed, ignited, long-fiber asbestos (amphibole type) should be used. Cut 125 g into 1-cm lengths, and separate the heavily clumped pieces by hand. Mix with 2 l water and 1 l conc. HCl in a 4-l beaker, and let stand with occasional stirring for 3–4 days. Decant through an 8-inch diameter Büchner funnel (use no paper) and wash with $\frac{1}{2}$ -l water. Add this asbestos to 3 l of 2% NaOH in a 4-l beaker, and let stand 6–8 hours. Decant through Büchner funnel (use no paper). Wash with $\frac{1}{2}$ l of 4–6 M HCl, and then with water until free of acid. Take up this washed asbestos in 3 l water to give the shelf reagent. To prepare Gooch crucibles, the shelf reagent should be diluted about threefold.

This is the minimum treatment that asbestos should receive for filtering ordinary acidic and basic solutions. For some filtrations special pretreatment may be required, which should be given in the directions for analysis.

Bromine water, saturated. Add 32 g (10.3 ml) bromine to 1 l water, and swirl well to dissolve. This gives a 0.2 M solution, which is very nearly saturated at room temperature.

Buffer solution, pH 4 (0.050 M KHP). Dissolve 102 g potassium acid phthalate in 10.0 l distilled water that has been boiled and cooled. As a preservative, add 0.6 g thymol. Store in a bottle equipped with a siphon, so that small portions may be conveniently withdrawn. The pH of this solution is 4.00–4.01 (20–30°C).

Buffer solution, pH 5 (0.5 M HAc–0.5 M NaAc). Dissolve 29 ml glacial HAc and 68 g NaAc \cdot 3H₂O, and make up to 1 l with distilled water. Dispense from 200-ml dropper-top bottles.

Buffer solution, pH 10 (NH₃–NH₄Cl). Dissolve 32 g of NH₄Cl in 100 ml water, add 285 ml conc. NH₃, and dilute to 500 ml. Dispense from 200-ml dropper-top bottles.

Dextrin (1%). Dissolve 10 g dextrin in 1 l of water and boil for a few minutes. Cool, and add 1 g thymol as a preservative. Permit any residue to settle overnight, and decant the clear solution.

Oxalate wash solution (0.1 M H₂C₂O₄–0.1 M (NH₄)₂C₂O₄). Dissolve 12.6 g H₂C₂O₄ \cdot 2H₂O and 28.4 g (NH₄)₂C₂O₄ \cdot H₂O in 1 l of water. Permit to stand overnight, and filter off any precipitate. Store the clear solution in a plastic bottle. For washing CaC₂O₄ precipitates, dilute this solution about tenfold.

Stannous chloride (0.67 M SnCl₂–6 M HCl). Dissolve 150 g SnCl₂ \cdot 2H₂O in 500 ml conc. HCl. Add water to make 1 l. Keep a few pieces of mossy tin in the reagent bottle to prevent oxidation.

V. Solubility Products *

Substance	Temp. (°C)	pK_s°	K_s°
ARSENATES			
† Ag ₃ AsO ₄	20°	21	10 ⁻²¹
† AlAsO ₄	22°	15.80	1.58 x 10 ⁻¹⁶
† Ba ₃ (AsO ₄) ₂	20°	50.11	7.8 x 10 ⁻⁵¹
† BiAsO ₄	20°	9.36	4.4 x 10 ⁻¹⁰
† Ca ₃ (AsO ₄) ₂	20°	18.17	6.8 x 10 ⁻¹⁹
† Cd ₃ (AsO ₄) ₂	20°	32.66	2.7 x 10 ⁻³³
† Co ₃ (AsO ₄) ₂	20°	28.12	7.6 x 10 ⁻²⁹
† CrAsO ₄	22°	20.11	7.8 x 10 ⁻²¹
† Cu ₃ (AsO ₄) ₂	20°	35.12	7.6 x 10 ⁻³⁶
† FeAsO ₄	20°	20.24	5.8 x 10 ⁻²¹
† Mg ₃ (AsO ₄) ₂	20°	19.68	2.1 x 10 ⁻²⁰
† Mn ₃ (AsO ₄) ₂	20°	28.72	1.91 x 10 ⁻²⁹
† Ni ₃ (AsO ₄) ₂	20°	25.51	3.1 x 10 ⁻²⁶
† Pb ₃ (AsO ₄) ₂	20°	35.39	4.1 x 10 ⁻³⁶
† Sr ₃ (AsO ₄) ₂	20°	17.9	1.3 x 10 ⁻¹⁸
† UO ₂ (HAsO ₄)	20°	10.50	3.2 x 10 ⁻¹¹
† Zn ₃ (AsO ₄) ₂	20°	28	10 ⁻²⁸
BROMATES			
AgBrO ₃	25°	4.27	5.4 x 10 ⁻⁵
† TlBrO ₃	20°	4.1	8 x 10 ⁻⁵
BROMIDES			
AgBr	25°	12.31	4.9 x 10 ⁻¹³
Hg ₂ Br ₂ †	25°	22.23	5.9 x 10 ⁻²³
† PbBr ₂	25°	4.56	2.8 x 10 ⁻⁵
TlBr	25°	5.46	3.5 x 10 ⁻⁶
CARBONATES			
† Ag ₂ CO ₃	25°	11.25	5.6 x 10 ⁻¹²
BaCO ₃	25°	8.29	5.1 x 10 ⁻⁹
CaCO ₃	25°	8.14	7.2 x 10 ⁻⁹
FeCO ₃	25°	10.46	3.5 x 10 ⁻¹¹
Hg ₂ CO ₃ †	25°	16.05	8.9 x 10 ⁻¹⁷
MgCO ₃	25°	4.5	3 x 10 ⁻⁵
† MnCO ₃	rt	10.4	4 x 10 ⁻¹¹
† NiCO ₃	25°	8.18	6.6 x 10 ⁻⁹
† PbCO ₃	18°	13.2	6 x 10 ⁻¹⁴
SrCO ₃	25°	9.4	4 x 10 ⁻¹⁰
ZnCO ₃	20°	10.84	1.45 x 10 ⁻¹¹

* For accuracy of solubility-product calculations, see page 711.

Parentetical numbers after hydroxides are approximate pK_a values for the first acid ionization constants of the metal ions:

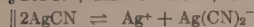


Symbols:

- rt Room temperature; not well defined.
- † These values are not activity products, since they were measured in solutions of finite or variable ionic strengths.
- ‡ Ionization into Hg₂²⁺ for mercurous salts, or into Hg(SCN)₄²⁻ for thiocyanomercurates.

V. Solubility Products—Cont.

Substance	Temp. (°C)	pK_s°	K_s°
CHLORIDES			
AgCl	25°	9.75	1.78×10^{-10}
† BiOCl‡	20°	6.68	2.1×10^{-7}
CuCl	25°	5.92	1.20×10^{-6}
Hg ₂ Cl ₂ ‡	25°	17.88	1.32×10^{-18}
PbCl ₂	25°	4.00	1.00×10^{-4}
TlCl	25°	3.76	1.74×10^{-4}
CHROMATES			
Ag ₂ CrO ₄	25°	11.89	1.29×10^{-12}
BaCrO ₄	25°	9.93	1.18×10^{-10}
CuCrO ₄	25°	5.51	4.9×10^{-6}
Hg ₂ CrO ₄ ‡	25°	8.70	2.0×10^{-9}
† PbCrO ₄	18°	13.75	1.78×10^{-14}
† SrCrO ₄	rt	4.44	3.6×10^{-5}
Tl ₂ CrO ₄	25°	12.01	9.8×10^{-13}
CYANATES			
AgCNO	19°	6.64	2.3×10^{-7}
CYANIDES			
† AgCN	rt	15.92	1.21×10^{-16}
† Hg ₂ (CN) ₂ ‡	rt	39.3	5×10^{-40}
FERROCYANIDES			
† Cd ₂ Fe(CN) ₆	25°	16.49	3.2×10^{-17}
† Co ₂ Fe(CN) ₆	25°	14.74	1.82×10^{-15}
† Cu ₂ Fe(CN) ₆	25°	15.89	1.29×10^{-16}
† Fe ₄ [Fe(CN) ₆] ₃	25°	40.52	3.0×10^{-41}
† Ga ₄ [Fe(CN) ₆] ₃	25°	33.82	1.51×10^{-34}
† In ₄ [Fe(CN) ₆] ₃	25°	43.72	1.91×10^{-44}
† Mn ₂ Fe(CN) ₆	25°	12.10	7.9×10^{-13}
† Ni ₂ Fe(CN) ₆	25°	14.89	1.29×10^{-15}
† Pb ₂ Fe(CN) ₆	25°	14.46	3.5×10^{-15}
† (UO ₂) ₂ Fe(CN) ₆	25°	13.15	7.1×10^{-14}
† Zn ₂ Fe(CN) ₆	25°	15.39	4.1×10^{-16}
FLUORIDES			
BaF ₂	25°	5.98	1.05×10^{-6}
CaF ₂	25°	10.41	3.9×10^{-11}
PbF ₂	25°	7.51	3.1×10^{-8}
SrF ₂	25°	8.57	2.7×10^{-9}
HYDROXIDES			
† AgOH (10)	25°	8.0	1.0×10^{-8}
† Al(OH) ₃ (5)	rt	31.7	2×10^{-32}
† Be(OH) ₂ (7)	rt	17.7	2×10^{-18}
† Bi(OH) ₃ (2)	rt	30	10^{-30}
Cd(OH) ₂ (10)	20°	13.5 (active)	3×10^{-14}
		14.2 (aged)	6×10^{-15}



V. Solubility Products—Cont.

Substance	Temp. (°C)	pK_s°	K_s°
HYDROXIDES—Cont.			
† Ce(OH) ₃ (9)	18°	22.3	5 × 10 ⁻²³
Co(OH) ₂ (12)	25°	14.2 (blue)	6 × 10 ⁻¹⁵
		14.8 (pink, fresh)	2 × 10 ⁻¹⁵
		15.7 (pink, aged)	2 × 10 ⁻¹⁶
Co(OH) ₃ (2)	25°	43	10 ⁻⁴³
Cr(OH) ₃ (4)	25°	30.1	8 × 10 ⁻³¹
Cu(OH) ₂ (7)	25°	19.5	3 × 10 ⁻²⁰
Fe(OH) ₂ (8)	25°	15.1	8 × 10 ⁻¹⁶
Fe(OH) ₃ (2)	18°	37.50	3.2 × 10 ⁻³⁸
† Ga(OH) ₃ (3)	rt	35	10 ⁻³⁵
Hg(OH) ₂ (3)	25°	25.2	6 × 10 ⁻²⁶
In(OH) ₃ (4)	18°	33.9	1.3 × 10 ⁻³⁴
† La(OH) ₃ (7)	rt	20	10 ⁻²⁰
Mg(OH) ₂ (13)	25°	10.95	1.12 × 10 ⁻¹¹
Mn(OH) ₂ (11)	22°	12.35	4.5 × 10 ⁻¹³
Ni(OH) ₂ (10)	25°	14.7 (active)	2 × 10 ⁻¹⁵
		17.2 (aged)	6 × 10 ⁻¹⁸
Pb(OH) ₂ (8)	rt	19.8	1.6 × 10 ⁻²⁰
Pd(OH) ₂	25°	31	10 ⁻³¹
† Sn(OH) ₂ (3)	25°	25	10 ⁻²⁵
Th(OH) ₄ (4)	25°	39	10 ⁻³⁹
TiO(OH) ₂	25°	29	10 ⁻²⁹
† Ti(OH) ₃ (1)	25°	41	10 ⁻⁴¹
VO(OH) ₂ (6)	25°	22.13	7.4 × 10 ⁻²³
† Y(OH) ₃ (8)	25°	22.80	1.58 × 10 ⁻²³
Zn(OH) ₂ (9)	25°	16	10 ⁻¹⁶
† ZrO(OH) ₂	25°	25.5	3 × 10 ⁻²⁶
IODATES			
AgIO ₃	25°	7.51	3.1 × 10 ⁻⁸
Ba(IO ₃) ₂	25°	8.82	1.51 × 10 ⁻⁹
Ca(IO ₃) ₂	25°	6.15	7.1 × 10 ⁻⁷
Ce(IO ₃) ₃	25°	9.48	3.3 × 10 ⁻¹⁰
Cu(IO ₃) ₂	25°	7.13	7.4 × 10 ⁻⁸
Hg ₂ (IO ₃) ₂ †	25°	16	10 ⁻¹⁶
La(IO ₃) ₃	25°	10	10 ⁻¹⁰
Pb(IO ₃) ₂	25°	12.53	2.9 × 10 ⁻¹³
Sr(IO ₃) ₂	25°	6.48	3.3 × 10 ⁻⁷
TiIO ₃	25°	5.51	3.1 × 10 ⁻⁶
IODIDES			
AgI	25°	16.01	9.8 × 10 ⁻¹⁷
† BiI ₃	20°	18.09	8.1 × 10 ⁻¹⁹
CuI	25°	11.96	1.10 × 10 ⁻¹²
Hg ₂ I ₂ †	25°	28.31	4.9 × 10 ⁻²⁹
PbI ₂	25°	8.98	1.05 × 10 ⁻⁹
† TlI	25°	7.24	5.8 × 10 ⁻⁸
OXALATES			
† Ag ₂ C ₂ O ₄	rt	11.05	8.9 × 10 ⁻¹²
BaC ₂ O ₄	25°	6.80	1.60 × 10 ⁻⁷
CaC ₂ O ₄	25°	8.73	1.86 × 10 ⁻⁹
† CuC ₂ O ₄	rt	7.5	3 × 10 ⁻⁸

V. Solubility Products—Cont.

Substance	Temp. (°C)	pK_s°	K_s°
OXALATES—Cont.			
$\text{La}_2(\text{C}_2\text{O}_4)_3$	25°	27.70	2.0×10^{-28}
MgC_2O_4	25°	6.15	7.1×10^{-7}
† PbC_2O_4	rt	10.57	2.7×10^{-11}
PHOSPHATES			
† Ag_3PO_4	rt	19.9	1.2×10^{-20}
† AlPO_4	19°	18.24	7.2×10^{-19}
† BiPO_4	19°	22.89	1.38×10^{-23}
† $\text{Ca}_3(\text{PO}_4)_2$	rt	28	10^{-28}
$\text{Ca}(\text{HPO}_4)_2$	25°	6.57	2.7×10^{-7}
† CrPO_4	19°	17.0 (violet)	1.0×10^{-17}
		22.6 (green)	3×10^{-23}
† FePO_4	19°	21.9	1.2×10^{-22}
† $\text{Hg}_2(\text{HPO}_4)_2$	25°	14	10^{-14}
$\text{Pb}_3(\text{PO}_4)_2$	25°	44	10^{-44}
† $\text{Pb}(\text{HPO}_4)$	rt	9.7	2×10^{-10}
† $\text{Th}_3(\text{PO}_4)_4$	19°	70	10^{-70}
† $\text{Th}(\text{HPO}_4)_2$	19°	20	10^{-20}
SULFATES			
Ag_2SO_4	25°	4.77	1.70×10^{-5}
BaSO_4	25°	10.00	1.00×10^{-10}
CaSO_4	25°	5.92	1.20×10^{-6}
Hg_2SO_4 †	25°	6.15	7.1×10^{-7}
PbSO_4	25°	7.77	1.70×10^{-8}
RaSO_4	25°	10.37	4.3×10^{-11}
SrSO_4	25°	6.49	3.2×10^{-7}
SULFIDES (W1)			
Ag_2S	25°	48.96 (beta)	1.1×10^{-49}
		49.17 (alpha)	6.8×10^{-50}
Bi_2S_3	25°	96.17	6.8×10^{-97}
CdS	25°	26.11	7.8×10^{-27}
Ce_2S_3	25°	10.12	7.7×10^{-11}
CoS	25°	20.23	5.9×10^{-21}
		22.06	8.7×10^{-23}
Co_2S_3	25°	123.58	2.6×10^{-124}
Cu_2S	25°	47.80	1.6×10^{-48}
CuS	25°	35.06	8.7×10^{-36}
FeS	25°	17.31	4.9×10^{-18}
Fe_2S_3	25°	34.85	1.4×10^{-35}
Hg_2S †	25°	43.24	5.8×10^{-44}
HgS	25°	51.07	8.6×10^{-52}
La_2S_3	25°	12.60	2.5×10^{-13}
MnS	25°	13.27 (green)	5.4×10^{-14}
		14.29 (pptd.)	5.1×10^{-15}
NiS	25°	20.74	1.8×10^{-21}
PbS	25°	27.08	8.4×10^{-28}
PtS	25°	71.10	8.0×10^{-72}
SnS	25°	24.92	1.2×10^{-25}
Ti_2S	25°	19.12	7.5×10^{-20}
ZnS	25°	20.96 (pptd.)	1.1×10^{-21}
		21.70 (Wurtzite)	2.0×10^{-22}
		24.06 (Sphalerite)	8.8×10^{-25}

V. Solubility Products—Cont.

Substance	Temp. (°C)	pK_s°	K_s°
THIOCYANATES			
AgSCN	25°	11.97	1.07×10^{-12}
† CuSCN	25°	14.32	4.8×10^{-15}
† Hg ₂ (SCN) ₂ ‡	25°	19.74	1.82×10^{-20}
† Pb(SCN) ₂	25°	4.70	2.0×10^{-5}
† TlSCN	25°	3.15	7.1×10^{-4}
THIOCYANO MERCURATES			
CoHg(SCN) ₄ ‡	20°	5.82	1.51×10^{-6}
† ZnHg(SCN) ₄ ‡	rt	6.66	2.2×10^{-7}

VI. Hydrated Ion Diameters and Activity Coefficients (25°C) *†

ION	ION SIZE α , Å	IONIC STRENGTH (From Concentrations in Moles per Liter)							
		0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.10
UNIVALENT IONS									
H ₃ O	9	.975	.967	.950	.933	.914	.88	.86	.83
	8	.975	.966	.949	.931	.912	.880	.85	.82
	7	.975	.965	.948	.930	.909	.875	.845	.81
Li	6	.975	.965	.948	.929	.907	.87	.835	.80
	5	.975	.964	.947	.928	.904	.865	.83	.79
Na, CdCl, ClO ₂ , IO ₃ , HCO ₃ , H ₂ PO ₄ , HSO ₃ , H ₂ AsO ₄ , Co(NH ₃) ₄ (NO ₂) ₂	4.5	.975	.964	.947	.928	.902	.86	.82	.775
	4	.975	.964	.947	.927	.901	.855	.815	.77
OH, F, SCN, OCN, HS, ClO ₃ , ClO ₄ , BrO ₃ , IO ₄ , MnO ₄	3.5	.975	.964	.946	.926	.900	.855	.81	.76
	3	.975	.964	.945	.925	.899	.85	.805	.755
K, Cl, Br, I, CN, NO ₂ , NO ₃	3	.975	.964	.945	.925	.899	.85	.805	.755
Rb, Cs, NH ₄ , Tl, Ag	2.5	.975	.964	.945	.924	.898	.85	.80	.75
DIVALENT IONS									
Mg, Be	8	.906	.872	.813	.755	.69	.595	.52	.45
	7	.906	.872	.812	.755	.685	.58	.50	.425
Ca, Cu, Zn, Sn, Mn, Fe, Ni, Co	6	.905	.870	.809	.749	.675	.57	.485	.405
Sr, Ba, Cd, Hg, S, S ₂ O ₄ , WO ₄	5	.903	.868	.805	.744	.67	.555	.465	.38
Pb, CO ₃ , SO ₃ , MoO ₄ , Co(NH ₃) ₅ Cl, Fe(CN) ₅ NO	4.5	.903	.867	.805	.742	.665	.55	.455	.37
Hg ₂ , SO ₄ , S ₂ O ₃ , S ₂ O ₆ , S ₂ O ₈ , SeO ₄ , CrO ₄ , HPO ₄	4	.903	.867	.803	.740	.660	.545	.445	.355
* Data taken from J. Kielland, <i>Journal of the American Chemical Society</i> , 59, 1675 (1937), Table II, with permission of the copyright owner, the American Chemical Society.									
† α , Å	ORGANIC UNIVALENT IONS								
8	Diphenyl acetate, (C ₆ H ₅) ₂ CH·COO; tetrapropylammonium, (C ₃ H ₇) ₄ N								
7	Picrate, (NO ₂) ₃ C ₆ H ₂ O; tripropylammonium, (C ₃ H ₇) ₃ NH; methoxybenzoate, CH ₃ O·C ₆ H ₄ ·COO								
6	Benzoate, C ₆ H ₅ COO; hydroxybenzoate, C ₆ H ₄ OHCOO; chlorobenzoate, C ₆ H ₄ ClCOO; phenylacetate, C ₆ H ₅ ·CH ₂ ·COO; allyl formate, CH ₂ :CH·CH ₂ ·COO; isovalerate, (CH ₃) ₂ CH·CH ₂ ·COO; tetraethylammonium, (C ₂ H ₅) ₄ N; dipropylammonium, (C ₃ H ₇) ₂ NH ₂								
5	Dichloroacetate, Cl ₂ CH·COO; trichloroacetate, Cl ₃ C·COO; triethylammonium, (C ₂ H ₅) ₃ NH; propylammonium, C ₃ H ₇ NH ₃								
4.5	Acetate, CH ₃ COO; chloroacetate, ClCH ₂ ·COO; tetramethylammonium, (CH ₃) ₄ N; diethylammonium, (C ₂ H ₅) ₂ NH ₂ ; aminoacetate, NH ₂ ·CH ₂ ·COO								
4	Trimethylammonium, (CH ₃) ₃ NH; ethylammonium, C ₂ H ₅ NH ₃ ; glycyl, HOOC·CH ₂ ·NH ₃								
3.5	Formate, HCOO; dihydrogencitrate, C ₆ H ₅ O ₇ H ₂ ; methylammonium, CH ₃ NH ₃ ; dimethylammonium, (CH ₃) ₂ NH ₂								
ORGANIC DIVALENT IONS									
7	Suberate, (CH ₂) ₆ (COO) ₂ ; pimelate, (CH ₂) ₅ (COO) ₂								
6	Phthalate, C ₆ H ₄ (COO) ₂ ; glutarate, (CH ₂) ₃ (COO) ₂ ; adipate, (CH ₂) ₄ (COO) ₂								
5	Succinate, (CH ₂) ₂ (COO) ₂ ; malonate, CH ₂ (COO) ₂ ; tartrate, (CHOHCOO) ₂								
4.5	Oxalate, (COO) ₂ ; monohydrogen citrate, C ₆ H ₅ O ₇ H								
ORGANIC TRIVALENT IONS									
5	Citrate, C ₆ H ₅ O ₇								

* Data taken from J. Kielland, *Journal of the American Chemical Society*, 59, 1675 (1937), Table II, with permission of the copyright owner, the American Chemical Society.

VI. Hydrated Ion Diameters and Activity Coefficients (25°C)—Cont.

ION	ION SIZE α , Å	IONIC STRENGTH (From Concentrations in Moles per Liter)							
		0.0005	0.001	0.0025	0.005	0.01	0.025	0.05	0.10
TRIVALENT IONS									
Al, Fe, Cr, Sc, Y, In, Rare earths	9	.802	.738	.632	.54	.445	.325	.245	.18
	6	.798	.731	.620	.52	.415	.28	.195	.13
	5	.796	.728	.616	.51	.405	.27	.18	.115
PO ₄ , Fe(CN) ₆ , Cr(NH ₃) ₆ , Co(NH ₃) ₆ , Co(NH ₃) ₅ H ₂ O	4	.796	.725	.612	.505	.395	.25	.16	.095
QUADRIVALENT IONS									
Th, Zr, Ce, Sn	11	.678	.588	.455	.35	.255	.155	.10	.065
	6	.670	.575	.43	.315	.21	.105	.055	.027
Fe(CN) ₆	5	.668	.57	.425	.31	.20	.10	.048	.021

VIIA. Ionization Constants of Inorganic Acids and Bases (25°C) *

Acid†	pK_a	K_a	pK_b	K_b
Ammonia, NH_4^+	9.26	5.5×10^{-10}	4.74	1.82×10^{-5}
Arsenic, H_3AsO_4	2.22	6.0×10^{-3}	11.88	1.67×10^{-12}
H_2AsO_4^-	6.98	1.05×10^{-7}	7.02	9.5×10^{-8}
HASO_4^{2-}	†11.4	4×10^{-12}	2.6	2.5×10^{-3}
Arsenious, H_3AsO_3	† 9.08	8.1×10^{-10}	4.92	1.23×10^{-5}
H_2AsO_3^-	†13.5	3×10^{-14}	0.5	0.3
Boric, HBO_2	9.19	6.5×10^{-10}	4.81	1.54×10^{-5}
Carbonic, H_2CO_3	† 6.46	3.5×10^{-7}	7.54	3.1×10^{-8}
HCO_3^-	†10.22	6.0×10^{-11}	3.78	1.67×10^{-4}
$\text{CO}_2(\text{g}) + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{CO}_3(\text{aq})$	† 1.47	3.4×10^{-2}		
Chlorous, HClO_2	1.97	1.07×10^{-2}	12.03	9.3×10^{-13}
Chromic, H_2CrO_4	-0.08	1.20	14.08	8.3×10^{-15}
HCrO_4^-	† 6.45	3.5×10^{-7}	7.55	2.8×10^{-8}
$\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2\text{HCrO}_4^-$	† 1.53	3.0×10^{-2}		
Cyanic, HCN	† 3.70	2.0×10^{-4}	10.30	5.0×10^{-11}
Ferrocyanic, $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$	3.0	1.0×10^{-3}	11.0	1.0×10^{-11}
$\text{HFe}(\text{CN})_6^{3-}$	4.25	5.6×10^{-5}	9.75	1.78×10^{-10}
Hydrazine, $\text{N}_2\text{H}_4 \cdot 2\text{H}^{2+}$	0.27	5.4×10^{-1}	13.73	1.86×10^{-14}
$\text{N}_2\text{H}_4 \cdot \text{H}^+$	7.94	1.15×10^{-8}	6.06	8.7×10^{-7}
Hydrocyanic, HCN	† 9.22	6.0×10^{-10}	4.78	1.66×10^{-5}
Hydrofluoric, HF	† 3.13	7.4×10^{-4}	10.87	1.35×10^{-11}
$\text{HF}_2^- \rightleftharpoons \text{HF} + \text{F}^-$	† 0.59	2.6×10^{-1}		
Hydrogen peroxide, H_2O_2	†11.75	1.78×10^{-12}	2.25	5.6×10^{-3}
Hydrogen selenide, H_2Se	3.81	1.55×10^{-4}	10.19	6.5×10^{-11}
HSe^-	11.0	1.0×10^{-11}	3.0	1.0×10^{-3}
Hydrogen sulfide, H_2S	6.99	1.02×10^{-7}	7.01	9.8×10^{-8}
HS^-	12.92	1.21×10^{-13}	1.08	8.3×10^{-2}
$\text{H}_2\text{S}(\text{g}) \rightleftharpoons \text{H}_2\text{S}(\text{aq})$	0.99	1.02×10^{-1}		
Hydrogen telluride, H_2Te	† 2.64	2.3×10^{-3}	11.36	4.4×10^{-12}
HTe^-	†11	10^{-11}	3	10^{-3}
Hydroxylamine, $\text{NH}_2\text{OH} \cdot \text{H}^+$	7.99	1.02×10^{-8}	6.01	9.8×10^{-7}
Hypobromous, HOBr	8.64	2.3×10^{-9}	5.36	4.4×10^{-6}
Hypochlorous, HOCl	7.50	3.2×10^{-8}	6.50	3.2×10^{-7}
Hypoiodous, HOI	11	10^{-11}	3	10^{-3}
Hypophosphorous, H_2PO_2^-	† 1.0	1.0×10^{-1}	13.0	1.0×10^{-13}
Iodic, HIO_3	0.77	1.70×10^{-1}	13.23	5.9×10^{-14}
Nitrous, HNO_2	† 3.35	4.5×10^{-4}	10.65	2.2×10^{-11}

* K_a is the acid ionization constant for the protonated species shown in the first column. K_b is the basic ionization constant for the conjugated base (not shown) of the protonated species shown in the first column. Thus, for monohydrogen arsenate, HASO_4^-

$$\text{HASO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{AsO}_4^{3-} \quad K_a, \text{ or } 4 \times 10^{-12} = \frac{[\text{H}_3\text{O}^+][\text{AsO}_4^{3-}]}{[\text{HASO}_4^-]}$$

$$\text{AsO}_4^{3-} + \text{H}_2\text{O} \rightleftharpoons \text{HASO}_4^- + \text{OH}^- \quad K_b, \text{ or } 2.5 \times 10^{-3} = \frac{[\text{HASO}_4^-][\text{OH}^-]}{[\text{AsO}_4^{3-}]}$$

Note that $K_a K_b = K_w$.

The table also contains a few other equilibrium constants that affect the pH. See chromic acid, hydrofluoric acid, etc. These equilibrium constants are given in the K_a column, even though they are not acid ionization constants.

Numerical values for the various equilibrium constants were taken principally from the work of Bjerrum *et al.* (B13).

† This table contains three substances that are commonly designated by their basic forms: ammonia, hydrazine, and hydroxylamine. For these, the basic names are given, but only the protonated forms (i.e., ammonium, etc.) are shown in the table.

‡ These values are not activity constants, since they were determined in solutions of finite or variable ionic strength.

VIIA. Ionization Constants of Inorganic Acids and Bases (25°C)—Cont.

Acid†	pK_a	K_a	pK_b	K_b
Periodic, H_5IO_6	3.29	5.1×10^{-4}	10.71	1.95×10^{-11}
$H_4IO_6^-$	6.69	2.0×10^{-7}	7.31	4.9×10^{-8}
$IO_4^- + 2H_2O \rightleftharpoons H_4IO_6^-$	1.60	2.5×10^{-2}		
Phosphoric, H_3PO_4	2.15	7.1×10^{-3}	11.85	1.41×10^{-12}
$H_2PO_4^-$	7.21	6.2×10^{-8}	6.79	1.62×10^{-7}
HPO_4^{2-}	12.36	4.4×10^{-13}	1.64	2.3×10^{-2}
Pyrophosphoric, $H_4P_2O_7$	0.83	1.48×10^{-1}	13.17	6.8×10^{-14}
$H_3P_2O_7^-$	2.36	4.4×10^{-3}	11.64	2.3×10^{-12}
$H_2P_2O_7^{2-}$	6.63	2.3×10^{-7}	7.37	4.3×10^{-8}
$HP_2O_7^{3-}$	9.29	5.1×10^{-10}	4.71	1.95×10^{-5}
Selenic, H_2SeO_4	2.03	9.3×10^{-3}	11.97	1.07×10^{-12}
Selenious, H_2SeO_3	‡ 2.51	3.1×10^{-3}	11.49	3.2×10^{-12}
$HSeO_3^-$	‡ 8.02	9.6×10^{-9}	5.98	1.05×10^{-6}
Silicic, H_4SiO_4	‡ 9.7	2×10^{-10}	4.3	5×10^{-5}
$H_3SiO_4^-$	‡12.2	6×10^{-13}	1.8	1.6×10^{-2}
Sulfuric, HSO_4^-	1.99	1.02×10^{-2}	12.01	9.8×10^{-13}
Sulfurous, H_2SO_3	1.76	1.74×10^{-2}	12.24	5.7×10^{-13}
HSO_3^-	7.20	6.3×10^{-8}	6.80	1.59×10^{-7}
$SO_2(g) + H_2O \rightleftharpoons H_2SO_3(aq)$	-0.09	1.23		
Telluric, H_2TeO_4	‡ 7.68	2.1×10^{-8}	6.32	4.8×10^{-7}
$HTeO_4^-$	‡10.39	4.1×10^{-11}	3.61	2.5×10^{-4}
Thiosulfuric, $H_2S_2O_3$	0.60	2.5×10^{-1}	13.40	4.0×10^{-14}
$HS_2O_3^-$	1.56	2.8×10^{-2}	12.44	3.6×10^{-13}

VII B. Ionization Constants of Organic Acids and Bases (25°C) *

Acid†	pK_a	K_a	pK_b	K_b
Acetic, $\text{CH}_3 \cdot \text{COOH}$	4.76	1.76×10^{-5}	9.24	5.7×10^{-10}
Acetylacetone, $\text{CH}_3 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{CH}_3$	‡ 8.98	1.05×10^{-9}	5.02	9.6×10^{-6}
Alanine, $\text{CH}_3 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COOH}$	2.34	4.6×10^{-3}	11.66	2.2×10^{-12}
$\text{CH}_3 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COO}^-$	9.87	1.35×10^{-10}	4.13	7.4×10^{-5}
Aniline, $\text{C}_6\text{H}_5\text{NH}_3^+$	4.62	2.4×10^{-5}	9.38	4.2×10^{-10}
Asparagine, $\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COOH}$	‡ 2.14	7.3×10^{-3}	11.86	1.38×10^{-12}
$\text{NH}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COO}^-$	‡ 8.85	1.41×10^{-9}	5.15	7.1×10^{-6}
Aspartic, $\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COOH}$	1.94	1.15×10^{-2}	12.06	8.7×10^{-13}
$\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COO}^-$	3.69	2.0×10^{-4}	10.31	4.9×10^{-11}
$^- \text{OOC} \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COO}^-$	9.61	2.5×10^{-10}	4.39	4.1×10^{-5}
Benzoic, $\text{C}_6\text{H}_5 \cdot \text{COOH}$	4.20	6.3×10^{-5}	9.80	1.59×10^{-10}
Chloroacetic, $\text{Cl} \cdot \text{CH}_2 \cdot \text{COOH}$	2.86	1.38×10^{-3}	11.14	7.2×10^{-12}
Citric, $\text{HOOC} \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{COOH}) \cdot \text{CH}_2 \cdot \text{COOH}$	3.08	8.3×10^{-4}	10.92	1.20×10^{-11}
$\text{HOOC} \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{COO}^-) \cdot \text{CH}_2 \cdot \text{COOH}$	4.76	1.74×10^{-5}	9.24	5.8×10^{-10}
$\text{HOOC} \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{COO}^-) \cdot \text{CH}_2 \cdot \text{COO}^-$	6.40	4.0×10^{-7}	7.60	2.5×10^{-8}
Cysteine, $\text{HS} \cdot \text{CH}_2 \cdot \text{CH}_2(\text{NH}_3^+) \cdot \text{COOH}$	‡ 1.96	1.10×10^{-2}	12.04	9.1×10^{-13}
$\text{HS} \cdot \text{CH}_2 \cdot \text{CH}_2(\text{NH}_3^+) \cdot \text{COO}^-$	‡ 8.54	2.9×10^{-9}	5.46	3.5×10^{-6}
$\text{HS} \cdot \text{CH}_2 \cdot \text{CH}_2(\text{NH}_2) \cdot \text{COO}^-$	‡ 10.51	3.1×10^{-11}	3.49	3.2×10^{-4}
1,2-diaminopropane, $\text{H}_3\text{C} \cdot \text{CH}(\text{NH}_3^+) \cdot \text{CH}_2 \cdot \text{NH}_3^+$	‡ 7.10	7.9×10^{-8}	6.90	1.26×10^{-7}
$\text{H}_3\text{C} \cdot \text{CH}(\text{NH}_2) \cdot \text{CH}_2 \cdot \text{NH}_3^+$	‡ 9.97	1.07×10^{-10}	4.03	9.3×10^{-5}
1,3-diaminopropane, $^+\text{NH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+$	‡ 8.98	1.05×10^{-9}	5.02	9.5×10^{-6}
$\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+$	‡ 10.64	2.3×10^{-11}	3.36	4.4×10^{-4}
Ethanolamine, $\text{HOCH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+$	‡ 9.60	2.5×10^{-10}	4.40	4.0×10^{-5}
Ethylamine, $\text{C}_2\text{H}_5 \cdot \text{NH}_3^+$	10.67	2.1×10^{-11}	3.33	4.7×10^{-4}
Ethylenediamine, $^+\text{NH}_3 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+$	‡ 7.42	3.8×10^{-8}	6.58	2.6×10^{-7}
$\text{NH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+$	‡ 10.14	7.2×10^{-11}	3.86	1.38×10^{-4}
EDTA (ethylenediaminetetraacetic acid), H_4Y	‡ 2.18	6.6×10^{-3}	11.82	1.51×10^{-12}
$\text{H}_4\text{Y} = \left[\text{CH}_2 \cdot \text{N} \begin{array}{l} \text{CH}_2 \cdot \text{COOH} \\ \text{CH}_2 \cdot \text{COOH} \end{array} \right]_2$	H_3Y^- ‡ 2.73	1.86×10^{-3}	11.27	5.4×10^{-12}
	H_2Y^{2-} ‡ 6.20	6.3×10^{-7}	7.80	1.59×10^{-8}
	HY^{3-} ‡ 10.0	1.0×10^{-10}	4.0	1.0×10^{-4}
Formic, HCOOH	3.77	1.70×10^{-4}	10.23	5.9×10^{-11}
Glutamic, $\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COOH}$	‡ 2.24	5.8×10^{-3}	11.76	1.74×10^{-12}
$\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COO}^-$	‡ 4.28	5.2×10^{-5}	9.72	1.91×10^{-10}
$^- \text{OOC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COO}^-$	‡ 9.79	1.62×10^{-10}	4.21	6.2×10^{-5}
Glyceric, $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}(\text{OH}) \cdot \text{COOH}$	‡ 3.52	3.0×10^{-4}	10.48	3.3×10^{-11}
Glycine, $^+\text{NH}_3 \cdot \text{CH}_2 \cdot \text{COOH}$	2.35	4.5×10^{-3}	11.65	2.2×10^{-12}
$^+\text{NH}_3 \cdot \text{CH}_2 \cdot \text{COO}^-$	9.78	1.66×10^{-10}	4.22	6.0×10^{-5}
Glycolic, $\text{HO} \cdot \text{CH}_2 \cdot \text{COOH}$	3.88	1.32×10^{-4}	10.12	7.6×10^{-11}
β -Hydroxypropionic, $\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$	3.73	1.86×10^{-4}	10.27	5.4×10^{-11}

* K_a is the ionization constant for the protonated species shown in the first column. K_b is the basic ionization constant for the conjugated base (not shown) of the protonated species shown in the first column. Thus, for glycine,

$$^+\text{NH}_3 \cdot \text{CH}_2 \cdot \text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_2 \cdot \text{CH}_2 \cdot \text{COO}^-$$

$$K_a, \text{ or } 1.66 \times 10^{-10} = \frac{[\text{H}_3\text{O}^+][\text{NH}_2 \cdot \text{CH}_2 \cdot \text{COO}^-]}{[^+\text{NH}_3 \cdot \text{CH}_2 \cdot \text{COO}^-]}$$



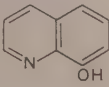
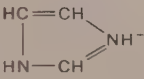
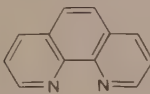
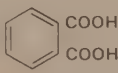
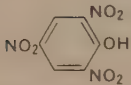
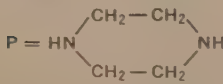

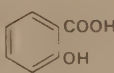
$$K_b, \text{ or } 6.0 \times 10^{-5} = \frac{[^+\text{NH}_3 \cdot \text{CH}_2 \cdot \text{COO}^-][\text{OH}^-]}{[\text{NH}_2 \cdot \text{CH}_2 \cdot \text{COO}^-]}$$

Note that $K_a K_b = K_w$.

Numerical values for the various constants were taken principally from the work of Bjerrum *et al.* (B13). † Some substances are commonly designated as bases. For these, the basic names are listed, but only the protonated forms are shown in the table. Thus, for ethanolamine ($\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_2$), only the protonated form ($\text{HO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NH}_3^+$) is shown.

‡ These values are not activity constants, since they were determined at finite or variable ionic strength.

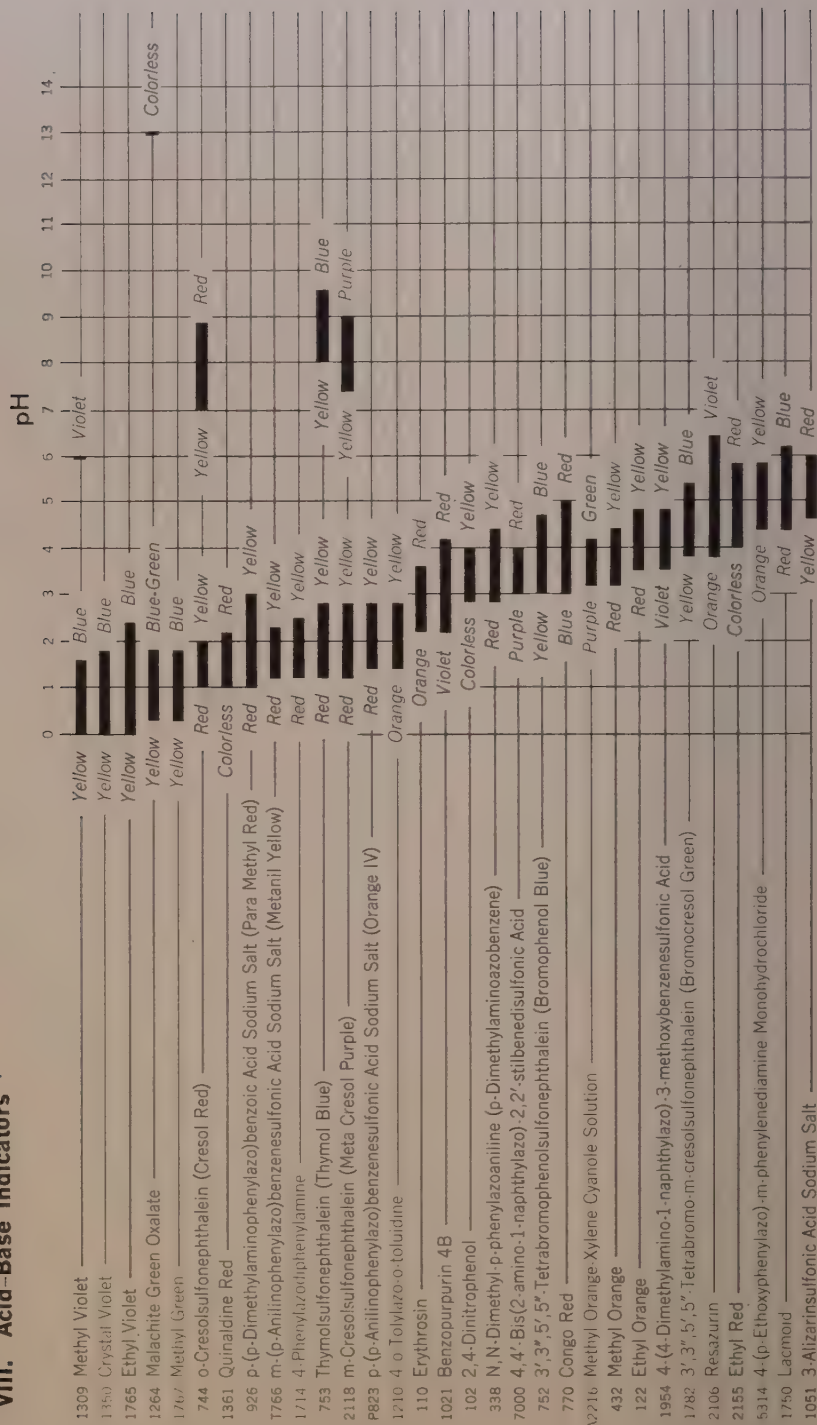
VII B. Ionization Constants of Organic Acids and Bases (25°C)—Cont.

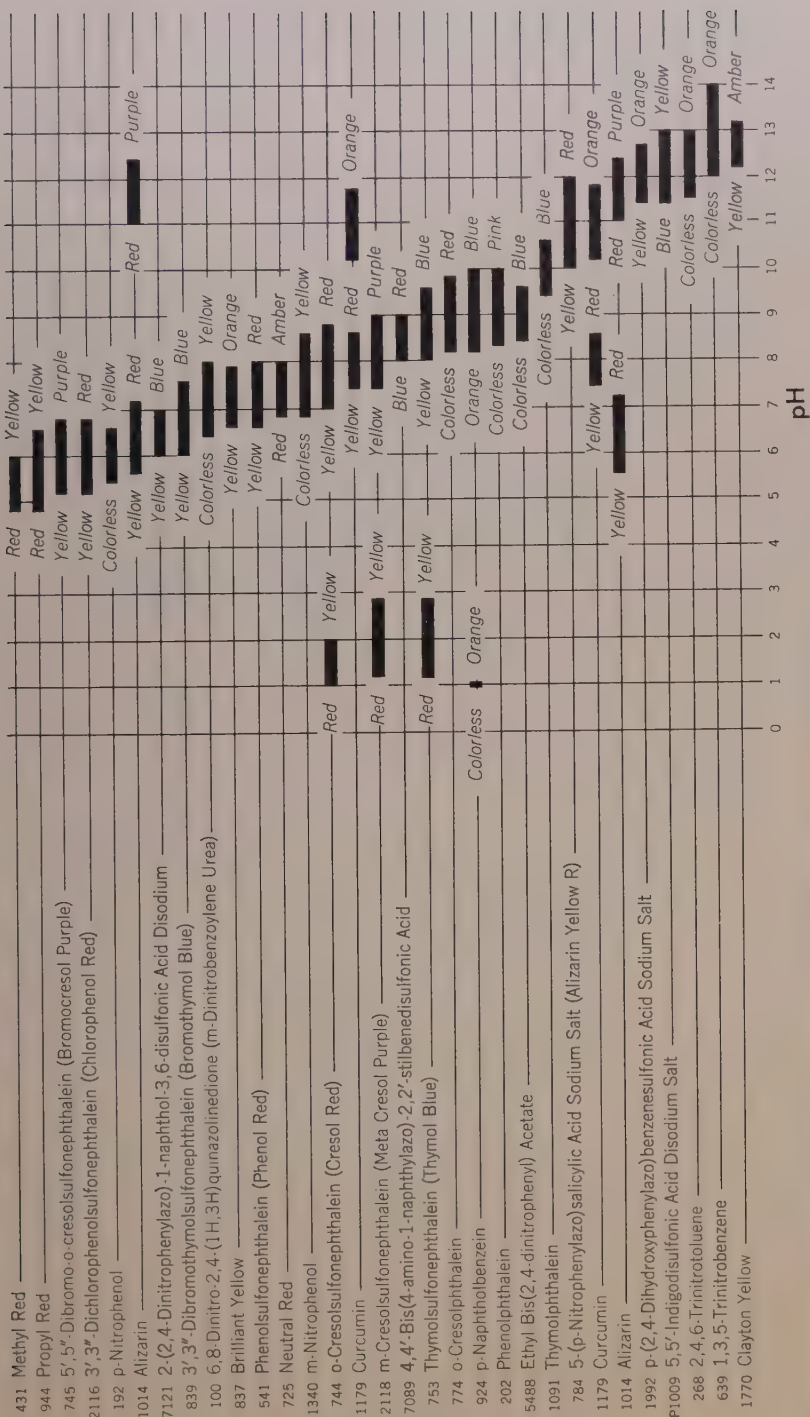
Acid†		pK_a	K_a	pK_b	K_b
8-Hydroxyquinoline, <div>HQ = </div>	H_2Q^+ ‡ 4.97 HQ ‡10.2	1.07×10^{-5} 6×10^{-11}	9.03 3.8	9.3×10^{-10} 1.6×10^{-4}	
Imidazole (glyoxaline), <div></div>	‡ 7.09	8.1×10^{-8}	6.91	1.23×10^{-7}	
Lactic, $H_3C \cdot CHOH \cdot COOH$	‡ 3.80	1.59×10^{-4}	10.20	6.3×10^{-11}	
Malonic, $HOOC \cdot CH_2 \cdot COOH$	‡ 2.82	1.51×10^{-3}	11.18	6.6×10^{-12}	
$HOOC \cdot CH_2 \cdot COO^-$	‡ 5.66	2.2×10^{-6}	8.34	4.6×10^{-9}	
Mercaptoacetic, $HS \cdot CH_2 \cdot COOH$	‡ 3.58	2.6×10^{-4}	10.42	3.8×10^{-11}	
$HS \cdot CH_2 \cdot COO^-$	‡ 9.78	1.66×10^{-10}	4.22	6.0×10^{-5}	
Mercaptoethylamine, $HS \cdot CH_2 \cdot CH_2 \cdot NH_3^+$	‡ 8.31	4.9×10^{-9}	5.69	2.0×10^{-6}	
$HS \cdot CH_2 \cdot CH_2 \cdot NH_2$	‡10.7	2×10^{-11}	3.3	5×10^{-4}	
Methylamine, $CH_3 \cdot NH_3^+$	‡10.72	1.91×10^{-11}	3.28	5.2×10^{-4}	
N-Methylaniline, $C_6H_5 \cdot NH_2^+ \cdot CH_3$	‡ 4.78	1.66×10^{-5}	9.22	6.0×10^{-10}	
Nitrilotriacetic, <div>$H_3T = N \equiv (\cdot CH_2 \cdot COOH)_3$</div>	H_3T ‡ 2.5 H_2T^- ‡ 2.8 HT^{2-} ‡10.2	3×10^{-3} 1.6×10^{-3} 6×10^{-11}	11.5 11.2 3.8	3×10^{-12} 6×10^{-12} 1.6×10^{-4}	
Oxalic, $HOOC \cdot COOH$	1.25	5.6×10^{-2}	12.75	1.78×10^{-13}	
$HOOC \cdot COO^-$	4.21	6.2×10^{-5}	9.79	1.62×10^{-10}	
o-Phenanthroline, <div>P = </div>	HP^+ ‡ 5.1	8×10^{-6}	8.9	1.3×10^{-9}	
Phenol, C_6H_5OH	‡ 9.98	1.05×10^{-10}	4.02	9.6×10^{-5}	
Phenylacetic, $C_6H_5 \cdot CH_2 \cdot COOH$	4.31	4.9×10^{-5}	9.69	2.0×10^{-10}	
Phthalic, <div>$H_2P =$</div>	H_2P 3.10 HP^- 5.40	8.0×10^{-4} 4.0×10^{-6}	10.90 8.60	1.26×10^{-11} 2.5×10^{-9}	
Picric, <div></div>	‡ 2.3	5×10^{-3}	11.7	2×10^{-12}	
Piperazine, <div>P = </div>	H_2P^{2+} ‡ 5.68 HP^+ ‡ 9.82	2.1×10^{-6} 1.51×10^{-10}	8.32 4.18	4.8×10^{-9} 6.6×10^{-5}	
Propionic, $H_3C \cdot CH_2 \cdot COOH$	4.87	1.35×10^{-5}	9.13	7.4×10^{-10}	
Pyridine, <div></div>	‡ 5.21	6.2×10^{-6}	8.79	1.62×10^{-9}	
Salicylic, <div>$H_2L =$</div>	H_2L 2.97 HL^- ‡13	1.07×10^{-3} 10^{-13}	11.03 1	9.3×10^{-12} 10^{-1}	

VII B. Ionization Constants of Organic Acids and Bases (25°C)—Cont.

Acid†	pK_a	K_a	pK_b	K_b
Succinic, $\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$	‡ 4.13	7.4×10^{-5}	9.87	1.35×10^{-10}
$\text{HOOC} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COO}^-$	‡ 5.38	4.2×10^{-6}	8.62	2.4×10^{-9}
Tartaric, $\text{HOOC} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COOH}$	‡ 2.70	2.0×10^{-3}	11.30	5.0×10^{-12}
$\text{HOOC} \cdot \text{CHOH} \cdot \text{CHOH} \cdot \text{COO}^-$	‡ 4.05	8.9×10^{-5}	9.95	1.12×10^{-10}
Trimethylamine, $(\text{H}_3\text{C})_3\text{NH}^+$	‡ 9.9	1.3×10^{-10}	4.1	8×10^{-5}
Tris (hydroxymethyl) aminomethane, $(\text{CH}_2\text{OH})_3\text{C} \cdot \text{NH}_3^+$	8.10	7.9×10^{-9}	5.90	1.26×10^{-6}
Tyrosine, $\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COOH}$	‡ 2.20	6.3×10^{-3}	11.80	1.58×10^{-12}
$\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_3^+) \cdot \text{COO}^-$	‡ 9.19	6.5×10^{-10}	4.81	1.55×10^{-5}
$\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_2 \cdot \text{CH}(\text{NH}_2) \cdot \text{COO}^-$	‡10.43	4.7×10^{-11}	3.57	2.7×10^{-4}

VIII. Acid-Base Indicators *





* Reproduced by permission of Distillation Products Industries, Division of Eastman Kodak Company.

IX. Standard Redox Potentials in Aqueous Solution (25°C) *

Couple†		E° (v)	Formal Potentials
$F_{2(g)} + 2H^+ + 2e$	\rightleftharpoons	2HF	3.06
$O_{3(g)} + 2H^+ + 2e$	\rightleftharpoons	$O_{2(g)} + H_2O$	2.07
$S_2O_8^{2-} + 2e$	\rightleftharpoons	$2SO_4^{2-}$	2.01
$H_2O_2 + 2H^+ + 2e$	\rightleftharpoons	$2H_2O$	1.77
$MnO_4^- + 4H^+ + 3e$	\rightleftharpoons	$MnO_{2(s)} + 2H_2O$	1.695
$Ce^{4+} + e$	\rightleftharpoons	Ce^{3+}	1.61
			1.7, 1 M HClO ₄ 1.61, 1 M HNO ₃ 1.44, 1 M H ₂ SO ₄ 1.23, 1 M HCl
$BrO_3^- + 6H^+ + 5e$	\rightleftharpoons	$\frac{1}{2}Br_{2(l)} + 3H_2O$	1.52
$MnO_4^- + 8H^+ + 5e$	\rightleftharpoons	$Mn^{2+} + 4H_2O$	1.51
$Cl_{2(g)} + 2e$	\rightleftharpoons	$2Cl^-$	1.3595
$Cr_2O_7^{2-} + 14H^+ + 6e$	\rightleftharpoons	$2Cr^{3+} + 7H_2O$	1.33
			1.10, 2 M H ₂ SO ₄ 1.09, 1 M HCl
$Ti^{3+} + 2e$	\rightleftharpoons	Ti^+	1.25
(B) $O_{3(g)} + H_2O + 2e$	\rightleftharpoons	$O_{2(g)} + 2OH^-$	1.24
$MnO_{2(s)} + 4H^+ + 2e$	\rightleftharpoons	$Mn^{2+} + 2H_2O$	1.23
			1.24, 1 M HClO ₄
$O_{2(g)} + 4H^+ + 4e$	\rightleftharpoons	$2H_2O$	1.229
$IO_3^- + 6H^+ + 5e$	\rightleftharpoons	$\frac{1}{2}I_{2(s)} + 3H_2O$	1.195
$Br_{2(l)} + 2e$	\rightleftharpoons	$2Br^-$	1.0652
$VO_2^+ + 2H^+ + e$	\rightleftharpoons	$VO^{2+} + H_2O$	1.00
			1.05, 4 M HCl 1.0, 1 M H ₂ SO ₄ 1.02, 1 M HClO ₄ 1.02, 1 M HCl
$HNO_2 + H^+ + e$	\rightleftharpoons	$NO_{(g)} + H_2O$	1.00
$NO_3^- + 3H^+ + 2e$	\rightleftharpoons	$HNO_2 + H_2O$	0.94
$2Hg_2^{2+} + 2e$	\rightleftharpoons	Hg_2^{2+}	0.920
$Ag^+ + e$	\rightleftharpoons	$Ag_{(s)}$	0.7991
			0.92, 1 M HNO ₃ 0.907, 1 M HClO ₄ 0.77, 1 M H ₂ SO ₄ 0.792, 1 M HClO ₄ 0.228, 1 M HCl 0.674, 1 M H ₂ SO ₄ 0.776, 1 M HClO ₄ 0.274, 1 M HCl 0.68, 1 M H ₂ SO ₄ 0.732, 1 M HClO ₄ 0.700, 1 M HCl
$Hg_2^{2+} + 2e$	\rightleftharpoons	$2Hg_{(l)}$	0.789
$Fe^{3+} + e$	\rightleftharpoons	Fe^{2+}	0.771
$O_{2(g)} + 2H^+ + 2e$	\rightleftharpoons	H_2O_2	0.682
$2HgCl_2 + 2e$	\rightleftharpoons	$Hg_2Cl_{2(s)} + 2Cl^-$	0.63
$H_3AsO_4 + 2H^+ + 2e$	\rightleftharpoons	$H_3AsO_3 + H_2O$	0.559
			0.577, 1 M HClO ₄ 0.577, 1 M HCl
$I_3^- + 2e$	\rightleftharpoons	$3I^-$	0.536
$I_2_{(s)} + 2e$	\rightleftharpoons	$2I^-$	0.5355
$Cu^+ + e$	\rightleftharpoons	$Cu_{(s)}$	0.521
$H_2MoO_4 + 2H^+ + e$	\rightleftharpoons	$MoO_2^+ + 2H_2O$	0.4
$VO^{2+} + 2H^+ + e$	\rightleftharpoons	$V^{3+} + H_2O$	0.361

* Data taken in part from W. M. Latimer, *The Oxidation States of the Elements and Their Potentials in Aqueous Solutions*, 2d ed. (Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1952), Appendix 1, and in part from E. H. Swift, *Introductory Quantitative Analysis* (Englewood Cliffs, N.J.: Prentice-Hall, Inc., 1950), Table 2, with permission of the publisher. Sources of Swift's Table 2 are given as follows: "Because values of the standard and the formal potentials are of fundamental importance in predicting the behavior of the elements in their various oxidation states, this table has not been restricted to the so-called common elements. Many of the standard potential values given below have been taken from Latimer, *Oxidation Potentials*, Prentice-Hall, 1938. A considerable number were collected or calculated by Dr. Clifford S. Garner from various sources; many of the formal potential values were calculated from measurements made over a number of years by selected students as part of the course in analytical chemistry at the California Institute of Technology."

† The symbol (B) preceding a couple indicates that the reaction occurs in basic solution. All other half-reactions occur in neutral or acidic solution.

IX. Standard Redox Potentials in Aqueous Solution (25°C)—Cont.

Couplet		E° (v)	Formal Potentials
$\text{Fe}(\text{CN})_6^{=} + e$	$\rightleftharpoons \text{Fe}(\text{CN})_6^{4-}$	0.36	0.48, 0.01 M HCl 0.56, 0.1 M HCl 0.72, 1 M H_2SO_4 0.72, 1 M HClO_4 0.71, 1 M HCl
$\text{Cu}^{2+} + 2e$	$\rightleftharpoons \text{Cu}_{(s)}$	0.337	
$\text{UO}_2^{2+} + 4\text{H}^+ + 2e$	$\rightleftharpoons \text{U}^{4+} + 2\text{H}_2\text{O}$	0.334	
$\text{Hg}_2\text{Cl}_{2(s)} + 2e$	$\rightleftharpoons 2\text{Hg}_{(l)} + 2\text{Cl}^-$	0.2676	0.282, 1 M KCl 0.246, sat. KCl
$\text{AgCl}_{(s)} + e$	$\rightleftharpoons \text{Ag}_{(s)} + \text{Cl}^-$	0.222	0.228, 1 M KCl
$\text{SO}_4^{=} + 4\text{H}^+ + 2e$	$\rightleftharpoons \text{H}_2\text{SO}_3 + \text{H}_2\text{O}$	0.17	
$\text{S}_4\text{O}_6^{=} + 2e$	$\rightleftharpoons 2\text{S}_2\text{O}_3^{=}$	0.17	
$\text{Cu}^{2+} + e$	$\rightleftharpoons \text{Cu}^+$	0.153	0.45, 1 M HCl
$\text{Sn}^{4+} + 2e$	$\rightleftharpoons \text{Sn}^{2+}$	0.15	0.14, 1 M HCl
$\text{TiO}^{2+} + 2\text{H}^+ + e$	$\rightleftharpoons \text{Ti}^{3+} + \text{H}_2\text{O}$	0.10	0.04, 1 M H_2SO_4
$\text{AgBr}_{(s)} + e$	$\rightleftharpoons \text{Ag}_{(s)} + \text{Br}^-$	0.095	
$2\text{H}^+ + 2e$	$\rightleftharpoons \text{H}_{2(g)}$	0.00	0.005, 1 M HNO_3 0.005, 1 M HClO_4 0.005, 1 M HCl
$\text{MoO}_2^{2+} + 4\text{H}^+ + 2e$	$\rightleftharpoons \text{Mo}^{3+} + 2\text{H}_2\text{O}$	0.0	
$\text{Pb}^{2+} + 2e$	$\rightleftharpoons \text{Pb}_{(s)}$	-0.126	-0.14, 1 M HClO_4
(B) $\text{CrO}_4^{=} + 4\text{H}_2\text{O} + 3e$	$\rightleftharpoons \text{Cr}(\text{OH})_{3(s)} + 5\text{OH}^-$	-0.13	
$\text{Sn}^{2+} + 2e$	$\rightleftharpoons \text{Sn}_{(s)}$	-0.136	-0.16, 1 M HClO_4
$\text{AgI}_{(s)} + e$	$\rightleftharpoons \text{Ag}_{(s)} + \text{I}^-$	-0.151	
$\text{CuI}_{(s)} + e$	$\rightleftharpoons \text{Cu}_{(s)} + \text{I}^-$	-0.185	
$\text{V}^{3+} + e$	$\rightleftharpoons \text{V}^{2+}$	-0.255	-0.21, 1 M HClO_4
(B) $\text{Ag}(\text{CN})_2^- + e$	$\rightleftharpoons \text{Ag}_{(s)} + 2\text{CN}^-$	-0.31	
$\text{Ti}^+ + e$	$\rightleftharpoons \text{Ti}_{(s)}$	-0.3363	
$\text{Cd}^{2+} + 2e$	$\rightleftharpoons \text{Cd}_{(s)}$	-0.403	
$\text{Cr}^{3+} + e$	$\rightleftharpoons \text{Cr}^{2+}$	-0.41	
$\text{Fe}^{2+} + e$	$\rightleftharpoons \text{Fe}_{(s)}$	-0.440	
$2\text{CO}_{2(g)} + 2\text{H}^+ + 2e$	$\rightleftharpoons \text{H}_2\text{C}_2\text{O}_4$	-0.49	
(B) $\text{Fe}(\text{OH})_{3(s)} + e$	$\rightleftharpoons \text{Fe}(\text{OH})_{2(s)} + \text{OH}^-$	-0.56	
$\text{Cr}^{3+} + 3e$	$\rightleftharpoons \text{Cr}_{(s)}$	-0.74	
$\text{Zn}^{2+} + 2e$	$\rightleftharpoons \text{Zn}_{(s)}$	-0.763	
(B) $2\text{H}_2\text{O} + 2e$	$\rightleftharpoons \text{H}_{2(g)} + 2\text{OH}^-$	-0.828	
$\text{Cr}^{2+} + 2e$	$\rightleftharpoons \text{Cr}_{(s)}$	-0.91	
$\text{Al}^{3+} + 3e$	$\rightleftharpoons \text{Al}_{(s)}$	-1.66	
$\text{Mg}^{2+} + 2e$	$\rightleftharpoons \text{Mg}_{(s)}$	-2.37	
(B) $\text{Mg}(\text{OH})_{2(s)} + 2e$	$\rightleftharpoons \text{Mg}_{(s)} + 2\text{OH}^-$	-2.69	
$\text{Na}^+ + e$	$\rightleftharpoons \text{Na}_{(s)}$	-2.714	
$\text{Ca}^{2+} + 2e$	$\rightleftharpoons \text{Ca}_{(s)}$	-2.87	
$\text{Ba}^{2+} + 2e$	$\rightleftharpoons \text{Ba}_{(s)}$	-2.90	

X. Selected Stability Constants *

Ligand	Reaction		K
Cl ⁻	Ag ⁺ + Cl ⁻	\rightleftharpoons AgCl	2.04 x 10 ³
	AgCl + Cl ⁻	\rightleftharpoons AgCl ₂ ⁻	93
	Ag ⁺ + 2Cl ⁻	\rightleftharpoons AgCl ₂ ⁻	1.91 x 10 ⁵
	Fe ³⁺ + Cl ⁻	\rightleftharpoons FeCl ²⁺	30
	FeCl ²⁺ + Cl ⁻	\rightleftharpoons FeCl ₂ ⁺	4
	FeCl ₂ ⁺ + Cl ⁻	\rightleftharpoons FeCl ₃	0.1
	Hg ²⁺ + Cl ⁻	\rightleftharpoons HgCl ⁺	5.9 x 10 ⁶
	HgCl ⁺ + Cl ⁻	\rightleftharpoons HgCl ₂	3.5 x 10 ⁶
	HgCl ₂ + Cl ⁻	\rightleftharpoons HgCl ₃ ⁻	5.1
	HgCl ₃ ⁻ + Cl ⁻	\rightleftharpoons HgCl ₄ ²⁻	11.2
CN ⁻	Ag ⁺ + 2CN ⁻	\rightleftharpoons Ag(CN) ₂ ⁻	6.3 x 10 ²⁰
	Cd ²⁺ + CN ⁻	\rightleftharpoons CdCN ⁺	1.51 x 10 ⁵
	CdCN ⁺ + CN ⁻	\rightleftharpoons Cd(CN) ₂	2.63 x 10 ⁴
	Cd(CN) ₂ + CN ⁻	\rightleftharpoons Cd(CN) ₃ ⁻	2.09 x 10 ⁴
	Cd(CN) ₃ ⁻ + CN ⁻	\rightleftharpoons Cd(CN) ₄ ²⁻	1.55 x 10 ³
	Cd ²⁺ + 4CN ⁻	\rightleftharpoons Cd(CN) ₄ ²⁻	1.29 x 10 ¹⁷
	Cu ²⁺ + 4CN ⁻	\rightleftharpoons Cu(CN) ₄ ²⁻	10 ²⁵
	Hg ²⁺ + 4CN ⁻	\rightleftharpoons Hg(CN) ₄ ²⁻	10 ⁴²
	Ni ²⁺ + 4CN ⁻	\rightleftharpoons Ni(CN) ₄ ²⁻	10 ²²
Ethylenediamine H ₂ N·CH ₂ ·CH ₂ ·NH ₂ , or E	Cu ²⁺ + E	\rightleftharpoons CuE ²⁺	2.3 x 10 ¹⁰
	CuE ²⁺ + E	\rightleftharpoons CuE ₂ ²⁺	8.5 x 10 ⁸
NH ₃	Ag ⁺ + NH ₃	\rightleftharpoons AgNH ₃ ⁺	2.04 x 10 ³
	AgNH ₃ ⁺ + NH ₃	\rightleftharpoons Ag(NH ₃) ₂ ⁺	7.8 x 10 ³
	Ag ⁺ + 2NH ₃	\rightleftharpoons Ag(NH ₃) ₂ ⁺	1.59 x 10 ⁷
	Cu ²⁺ + 4NH ₃	\rightleftharpoons Cu(NH ₃) ₄ ²⁺	2.0 x 10 ¹⁴
	Ni ²⁺ + 6NH ₃	\rightleftharpoons Ni(NH ₃) ₆ ²⁺	4.1 x 10 ⁸
	Zn ²⁺ + NH ₃	\rightleftharpoons ZnNH ₃ ²⁺	3.9 x 10 ²
	ZnNH ₃ ²⁺ + NH ₃	\rightleftharpoons Zn(NH ₃) ₂ ²⁺	2.1 x 10 ²
	Zn(NH ₃) ₂ ²⁺ + NH ₃	\rightleftharpoons Zn(NH ₃) ₃ ²⁺	102
	Zn(NH ₃) ₃ ²⁺ + NH ₃	\rightleftharpoons Zn(NH ₃) ₄ ²⁺	51
SCN ⁻	Fe ³⁺ + SCN ⁻	\rightleftharpoons FeSCN ²⁺	1.07 x 10 ³
	Hg ²⁺ + SCN ⁻	\rightleftharpoons HgSCN ⁺	3.0 x 10 ⁹
	HgSCN ⁺ + SCN ⁻	\rightleftharpoons Hg(SCN) ₂	2.0 x 10 ¹⁰
	Hg(SCN) ₂ + SCN ⁻	\rightleftharpoons Hg(SCN) ₃ ⁻	50
	Hg ²⁺ + 4SCN ⁻	\rightleftharpoons Hg(SCN) ₄ ²⁻	7.7 x 10 ²¹

* Stability constants in this table are taken largely from the compilation by Bjerrum *et al.* (B13). In general, the tabled values are not activity constants, and the conditions under which any value applies must be found by consulting the original literature.

Stability constants for 1:1 complexes between various metal ions and some polydentate chelating agents are given on pages 566-67, 575-76.

LIST OF REFERENCES

A classified list of analytical references is given in Chapter 24.

- A1** Adler, S. J., and Noyes, R. M., *Journal of the American Chemical Society*, **77**, 2036 (1955).
- A2** Agterdenbos, J., *Analytica Chimica Acta*, **15**, 429 (1956).
- A3** Ainsworth, A. W., *Industrial and Engineering Chemistry, Analytical Edition*, **11**, 572 (1939).
- A4** Allmand, A. J., Cunliffe, P. W., and Maddison, R. E. W., *Journal of the Chemical Society (London)*, **129**, 655 (1927).
- A5** Allport, N. L., and Keyser, J. W., *Colorimetric Analysis: Determinations of Clinical and Biochemical Significance*, 2d ed. Chapman and Hall, London, 1957.
- A6** Almer, H. G., *Journal of Research, National Bureau of Standards*, **64C**, 281 (1960).
- A7** Alter, C. M., and Thomas, D. S., *Industrial and Engineering Chemistry, Analytical Edition*, **12**, 525 (1940).
- A8** American Chemical Society, *Reagent Chemicals: American Chemical Society Specifications, 1955*. Washington, D.C., 1955.
- A9** American Chemical Society, *SYMPOSIUM ON THERMAL METHODS OF ANALYSIS*, 1960, *Analytical Chemistry*, **32**, 1558-95 (1960).
- A10** American Society for Testing and Materials, *ASTM Manual on Quality Control of Materials*. Technical Publication 15-C. Philadelphia, 1951.
- A11** American Society for Testing and Materials, *1958 Book of ASTM Standards*. Philadelphia, 1959-60. 10 vols. and suppl.
- A12** American Society for Testing and Materials, *Book of ASTM Methods for Chemical Analysis of Metals*. Philadelphia, 1960.
- A13** Andrews, L. W., *Journal of the American Chemical Society*, **29**, 275 (1907).
- A14** Association of Official Agricultural Chemists, *Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists*, 9th ed. (W. Horwitz, ed.). Washington, D.C., 1960.
- A15** Auerbach, F., and Smolczyk, E., *Zeitschrift für physikalische Chemie*, **110A**, 65 (1924).
- A16** Awtrej, A. D., and Connick, R. E., *Journal of the American Chemical Society*, **73**, 1341, 4546 (1951).
- B1** Bailar, J. C., *The Chemistry of Coordination Compounds*. Reinhold, New York, 1956.

- B2** Bard, A. J., and Simonsen, S. H., *Journal of Chemical Education*, **37**, 364 (1960).
- B3** Barnard, A. J., Broad, W. C., and Flaschka, H., *Chemist-Analyst*, **45**, 86 (1956); **46**, 18, 46, 76 (1957).
- B4** Barrer, R. M., Sixteenth International Congress of Pure and Applied Chemistry. *Experientia Supplement VII*, 113-33 (1957). Birkhauser, Basel, 1957.
- B5** Bates, R. G., *Electrometric pH Determinations*. Wiley, New York, 1954.
- B6** Bates, R. G., ELECTRODE POTENTIALS, in *Treatise on Analytical Chemistry*, Pt. I, Vol. 1, Ch. 9 (I. M. Kolthoff and P. J. Elving, eds.). Wiley, New York, 1959.
- B7** Belcher, R., Macdonald, A. M. G., and Parry, E., *Analytica Chimica Acta*, **16**, 524 (1957).
- B8** Benedetti-Pichler, A. A., *Industrial and Engineering Chemistry, Analytical Edition*, **8**, 373 (1936).
- B9** Benedetti-Pichler, A. A., *Essentials of Quantitative Analysis*. Ronald Press, New York, 1956.
- B10** Benedetti-Pichler, A. A., and Bogan, E. J., *Analytical Chemistry*, **27**, 1505 (1955).
- B11** Berl, W. G. (ed.), *Physical Methods in Chemical Analysis*. Academic Press, New York, 1950-61. 4 vols.
- B12** Bishop, E., *Analytica Chimica Acta*, **20**, 315 (1959).
- B13** Bjerrum, J., Schwarzenbach, G., and Sillen, G., *Stability Constants*. Special Publication No. 7. The Chemical Society, London, 1957-58. 2 vols.
- B14** Blaedel, W. J., Lewis, W. B., and Thomas, J. W., *Analytical Chemistry*, **24**, 509 (1952).
- B15** Blaedel, W. J., and Meloche, V. W., *Elementary Quantitative Analysis*. Harper, New York, 1957.
- B16** Blaedel, W. J., Meloche, V. W., and Ramsay, J. A., *Journal of Chemical Education*, **28**, 643 (1951).
- B17** Bobtelsky, M., *Heterometry*. Van Nostrand, New York, 1960.
- B18** Bognar, J., and Jellinek, O., *Acta Chimica Academiae Scientiarum Hungaricae*, **17**, 17 (1958).
- B19** Bolie, V. W., *Journal of Chemical Education*, **35**, 449 (1958).
- B20** Boltz, D. F. (ed.), *Colorimetric Determination of Nonmetals*. Wiley, New York, 1958.
- B21** Booth, H. S., and McIntyre, L., *Industrial and Engineering Chemistry, Analytical Edition*, **8**, 148 (1936).
- B22** Bower, J. H., *Journal of Research of the National Bureau of Standards*, **12**, 241 (1934).
- B23** Bradbury, R. B., *Analytical Chemistry*, **21**, 1139 (1949).
- B24** Bradstreet, R. B., *Analytical Chemistry*, **26**, 185 (1954).
- B25** Bridgman, P. W., *The Nature of Physical Theory*. Princeton University Press, Princeton, N.J., 1936.
- B26** Brinton, P. H. M.-P., *Journal of the American Chemical Society*, **41**, 1151 (1919).
- B27** Brunauer, S., *The Adsorption of Gases and Vapors*, Vol. 1 (Physical Adsorption). Princeton University Press, Princeton, N.J., 1943.
- B28** Buckley, H. E., *Crystal Growth*. Wiley, New York, 1951.

- B29** Budde, W. M., and Potempa, S. J., *Analytical Chemistry*, **22**, 1072 (1950).
- B30** Burgess, G. K., and Waltenberg, R. G., *Journal of Industrial and Engineering Chemistry*, **8**, 487 (1916).
- C1** Carmody, W. R., *Industrial and Engineering Chemistry, Analytical Edition*, **17**, 577 (1945).
- C2** Clark, G. L., Nash, L. K., and Fischer, R. B., *Quantitative Chemical Analysis*. Saunders, Philadelphia, 1949.
- C3** Clark, W. M., *Oxidation-Reduction Potentials of Organic Systems*. Williams and Wilkins, Baltimore, 1960.
- C4** Cohen, A. I., and Gordon, L., *Talanta*, **7**, 195 (1961).
- C5** Collins, E. M., and Menzies, A. W. C., *Journal of Physical Chemistry*, **40**, 379 (1936).
- C6** Cooper, M. D., *Analytical Chemistry*, **25**, 411 (1953).
- C7** Corner, M., *PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM ON MICRO-CHEMISTRY*, 1958 (p. 64). Pergamon Press, London, 1960.
- C8** Cram, D. J., and Hammond, G. S., *Organic Chemistry*. McGraw-Hill, New York, 1959.
- C9** Crestfield, A. M., *Analytical Chemistry*, **28**, 117 (1956).
- C10** Crouthamel, C. E. (ed.), *Applied Gamma-Ray Spectrometry*. Pergamon Press, New York, 1960.
- C11** Crowell, W. R., Hillis, T. E., Rittenberg, S. C., and Evenson, R. F., *Industrial and Engineering Chemistry, Analytical Edition*, **8**, 9 (1936).
- C12** Crumpler, T. B., and Yoe, J. H., *Chemical Computations and Errors*. Wiley, New York, 1940.
- C13** Czanderna, A. W., and Honig, J. M., *Analytical Chemistry*, **29**, 1206 (1957).
- D1** Daniels, F., and Alberty, R. A., *Physical Chemistry*, 2d ed. Wiley, New York, 1961.
- D2** Dean, R. B., and Dixon, W. J., *Analytical Chemistry*, **23**, 636 (1951).
- D3** Dekker, A. O., Levy, H. A., and Yost, D. M., *Journal of the American Chemical Society*, **59**, 2129 (1937).
- D4** Delahay, P., *Instrumental Analysis*. Macmillan, New York, 1957.
- D5** Dickinson, W. E., *Analytical Chemistry*, **30**, 992 (1958).
- D6** Diehl, H., and Smith, G. F., *Talanta*, **2**, 209 (1959).
- D7** Diehl, H., and Smith, G. F., *Talanta*, **2**, 382 (1959).
- D8** Dixon, W. J., and Massey, F. J., Jr., *Introduction to Statistical Analysis*, 2d ed. McGraw-Hill, New York, 1957.
- D9** Dubravcic, M., *Analyst*, **80**, 146, 295 (1955).
- D10** Duke, F. R., *MECHANISMS OF OXIDATION-REDUCTION REACTIONS, in Treatise on Analytical Chemistry*, Pt. I, Vol. 1, Ch. 15 (I. M. Kolthoff and P. J. Elving, eds.). Wiley, New York, 1959.
- D11** Duke, F. R., *Journal of Chemical Education*, **38**, 161 (1961).
- D12** Duval, C., *Analytical Chemistry*, **23**, 1271 (1951).
- D13** Duval, C., *Inorganic Thermogravimetric Analysis*. Elsevier, Amsterdam, Houston, 1953.
- E1** Elving, P. J., *Analytical Chemistry*, **22**, 962 (1950).
- E2** Erdey, L., Polos, L., and Gregorowicz, G., *Talanta*, **2**, 384 (1959).

- E3** Erdey, L., and Svehla, G., *Zeitschrift für analytische Chemie*, **154**, 406 (1957).
- F1** Feibush, A. M., Rowley, K., and Gordon, L., *Analytical Chemistry*, **30**, 1605 (1958).
- F2** Fine, L., and Wynne, E. A., *Microchemical Journal*, **3**, 515 (1959).
- F3** Fischer, R. B., *Analytical Chemistry*, **28**, (No. 12), 9A (1956).
- F4** Fischer, R. B., and Rhinehammer, T. B., *Analytical Chemistry*, **25**, 1544 (1953).
- F5** Flaschka, H. A., *EDTA Titrations*. Pergamon Press, New York, 1959.
- F6** Foulk, C. W., and Hollingsworth, M., *Journal of the American Chemical Society*, **45**, 1220 (1923).
- F7** Foulk, C. W., Moyer, H. V., and MacNevin, W. M., *Quantitative Chemical Analysis*. McGraw-Hill, New York, 1952.
- F8** Fowler, R. M., and Bright, H. A., *Journal of Research of the National Bureau of Standards*, **15**, 493 (1935).
- F9** French, D., and Edsall, J. T., *Advances in Protein Chemistry*, **2**, 278 (1945).
- F10** Fritz, J. J., *Journal of Chemical Education*, **30**, 442 (1953).
- F11** Fritz, J. S., and Hammond, G. S., *Quantitative Organic Analysis*. Wiley, New York, 1957.
- G1** Gage, J. C., *Analyst*, **82**, 219 (1957).
- G2** Goetz, C. A., and Wadsworth, E. P., *Analytical Chemistry*, **28**, 375 (1956).
- G3** Gordon, L., *Analytical Chemistry*, **24**, 459 (1952).
- G4** Gordon, L., Salutsky, M. L., and Willard, H. H., *Precipitation from Homogeneous Solutions*. Wiley, New York, 1959.
- G5** Gottlieb, O. R., *Analytica Chimica Acta*, **14**, 497 (1956).
- G6** Grunwald, E., *Analytical Chemistry*, **28**, 1112 (1956).
- H1** Hahn, O., *Applied Radiochemistry*. Cornell University Press, Ithaca, N.Y., 1936.
- H2** Halstead, P. E., and Moore, A. E., *Journal of the Chemical Society (London)*, 3873 (1957).
- H3** Hamilton, R. H., *Analytical Chemistry*, **25**, 399 (1953).
- H4** Harlow, G. A., Noble, C. M., and Wyld, G. E. A., *Analytical Chemistry*, **28**, 787 (1956).
- H5** Hayman, D. F., *Industrial and Engineering Chemistry, Analytical Edition*, **8**, 342 (1936).
- H6** Headridge, J. B., *Photometric Titrations*. Pergamon Press, New York, 1961.
- H7** Hill, U. T., *Industrial and Engineering Chemistry, Analytical Edition*, **19**, 932 (1947).
- H8** Hillebrand, W. F., Lundell, G. E. F., Bright, H. A., and Hoffman, J. I., *Applied Inorganic Analysis*, 2d ed. Wiley, New York, 1953.
- H9** Holler, A. C., *Analytical Chemistry*, **27**, 866 (1955).
- H10** Holth, T., *Analytical Chemistry*, **21**, 1221 (1949).
- H11** Hoover, T. B., and Hutchison, W., *Analytical Chemistry*, **29**, 518 (1957).
- H12** Hughes, R. H., *Annals of the New York Academy of Sciences*, **55**, 872 (1952).
- H13** Hull, D. E., *Analytical Chemistry*, **29**, 1202 (1957).

- H14 Hume, D. N., and Kolthoff, I. M., *Analytica Chimica Acta*, **16**, 415 (1957).
- H15 Hutner, S. H., Cury, A., and Baker, H., *Analytical Chemistry*, **30**, 849 (1958).
- I1 Issa, I. M., El-Aasser, A. A., and El-Merzibani, M. M., *Zeitschrift für analytische Chemie*, **178**, 12 (1960).
- I2 Ives, D. J. G., and Janz, G. J. (eds.), *Reference Electrodes*. Academic Press, New York, 1961.
- J1 James, T. H., *Journal of Physical Chemistry*, **46**, 1068 (1942).
- J2 Jamieson, G. S., *Volumetric Iodate Methods*. Chemical Catalog Co., New York, 1926.
- J3 Jander, G. (ed.), *Newer Volumetric Methods*, 4th ed. F. Enke, Stuttgart, Germany, 1956.
- J4 Jucker, H., *Analytica Chimica Acta*, **16**, 210 (1957).
- K1 Karsten, P., Kies, H. L., Van Engelen, H. Th. J., and deHoog, P., *Analytica Chimica Acta*, **12**, 64 (1955).
- K2 Katz, S., and Barr, J. T., *Analytical Chemistry*, **25**, 619 (1953).
- K3 Keyworth, D. A., and Hahn, R. B., *Analytical Chemistry*, **30**, 1343 (1958).
- K4 King, E. L., *Journal of Chemical Education*, **31**, 183 (1954).
- K5 King, J., *Analyst*, **77**, 8 (1952).
- K6 Kirk, P. L., *Analytical Chemistry*, **22**, 354 (1950).
- K7 Kirk, P. L., *Quantitative Ultramicroanalysis*. Wiley, New York, 1950.
- K8 Klein, D. H., and Gordon, L., *Talanta*, **1**, 334 (1958).
- K9 Knapp, L. F., *Transactions of the Faraday Society*, **17**, 457 (1921).
- K10 Koch, R. C., *Activation Analysis Handbook*. Academic Press, New York, 1960.
- K11 Kolthoff, I. M., *Journal of Physical Chemistry*, **40**, 1027 (1936).
- K12 Kolthoff, I. M., and Elmquist, R., *Journal of the American Chemical Society*, **53**, 1232 (1931).
- K13 Kolthoff, I. M., and Elving, P. J. (eds.), *Treatise on Analytical Chemistry*. Wiley, New York, 1959—. 10 vols.
- K14 Kolthoff, I. M., and Griffith, F. S., *Journal of Physical Chemistry*, **42**, 531 (1938).
- K15 Kolthoff, I. M., and Lingane, J. J., *Journal of the American Chemical Society*, **57**, 2126 (1935).
- K16 Kolthoff, I. M., and Livingston, R. S., *Industrial and Engineering Chemistry, Analytical Edition*, **7**, 209 (1935).
- K17 Kolthoff, I. M., and Rosenblum, C., *Journal of the American Chemical Society*, **56**, 1264 (1934).
- K18 Kolthoff, I. M., and Sandell, E. B., *Textbook of Quantitative Inorganic Analysis*, 3d ed. Macmillan, New York, 1952.
- K19 Kolthoff, I. M., and Stenger, V. A., *Volumetric Analysis*, 2d ed. Wiley, New York, 1942–57. 3 vols.
- K20 Korbl, J., and Pribl, R., *Collection of Czechoslovak Chemical Communications*, **22**, 1122 (1957).
- K21 Kunzler, J. E., *Analytical Chemistry*, **25**, 93 (1953).
- L1 Lachiver, F., *Annales de Chimie et de Physique, Series 12*, **10**, 92 (1955).

- L2 Laitinen, H. A., *Chemical Analysis*. McGraw-Hill, New York, 1960.
- L3 LaMer, V. K., and Dinegar, R. H., *Journal of the American Chemical Society*, **72**, 4847 (1950); **73**, 380 (1951).
- L4 Lange, N. A., *Handbook of Chemistry*, 10th ed. McGraw-Hill, New York, 1961.
- L5 Langer, A., *Analytical Chemistry*, **22**, 1288 (1950).
- L6 Latimer, W. M., *The Oxidation States of the Elements and Their Potentials in Aqueous Solution*, 2d ed. Prentice-Hall, Englewood Cliffs, N.J., 1952.
- L7 Leussing, D. L., SOLUBILITY, in *Treatise on Analytical Chemistry*, Pt. I, Vol. 1, Ch. 17 (I. M. Kolthoff and P. J. Elving, eds.). Wiley, New York, 1959.
- L8 Lewin, S., *The Solubility Product Principle*. Pitman, London, 1960.
- L9 Lewin, S. Z., *Journal of Chemical Education*, **36**, A7, A67 (1959).
- L10 Linde, H. W., Rogers, L. B., and Hume, D. N., *Analytical Chemistry*, **25**, 404 (1953).
- L11 Lingane, J. J., *Industrial and Engineering Chemistry, Analytical Edition*, **17**, 39 (1945).
- L12 Lingane, J. J., *Electroanalytical Chemistry*, 2d ed. Wiley, New York, 1958.
- L13 Lingane, J. J., and Karplus, R., *Industrial and Engineering Chemistry, Analytical Edition*, **18**, 191 (1946).
- L14 Lion, K. S., *Instrumentation for Scientific Research*. McGraw-Hill, New York, 1959.
- L15 Luder, W. F., and Zuffanti, S., *Electronic Theory of Acids and Bases*. Wiley, New York, 1946.
- L16 Lumb, E. C., and Winsor, P. A., *Analyst*, **77**, 1012 (1952).
- L17 Lundell, G. E. F., and Hoffman, J. I., *Journal of Research of the National Bureau of Standards*, **4**, 109 (1930).
- M1 McBride, R. S., *Journal of the American Chemical Society*, **34**, 393 (1912).
- M2 McEwen, D. J., and DeVries, T., *Analytical Chemistry*, **30**, 1889 (1958).
- M3 MacNevin, W. M., *The Analytical Balance: Its Care and Use*. McGraw-Hill, New York, 1959.
- M4 Mallinckrodt Chemical Works, ANALYTICAL REAGENT DATA (Subject: Potassium Acid Phthalate A. R. Primary Standard. Index: AR-3). St. Louis, Mo., 1949.
- M5 Malmstadt, H. V., and Gohrbandt, E. C., *Analytical Chemistry*, **26**, 442 (1954).
- M6 Manov, G. G., and Kirk, P. L., *Industrial and Engineering Chemistry, Analytical Edition*, **9**, 198 (1937).
- M7 Martell, A. E., and Calvin, M., *Chemistry of the Metal Chelate Compounds*. Prentice-Hall, Englewood Cliffs, N.J., 1952.
- M8 Martin, E. L., and Bentley, K. E., *Journal of Chemical Education*, **38**, 264 (1961).
- M9 Martin, R. B., *Analyst*, **80**, 318 (1955).
- M10 Matijevik, E., Kratochvil, J. P., and Kerker, M., *Journal of Chemical Education*, **38**, 397 (1961).
- M11 May, D., and Kolthoff, I. M., *Journal of Physical Chemistry*, **52**, 836 (1948).

- M12** Medalia, A. I., *Analytical Chemistry*, **27**, 1678 (1955).
- M13** Meites, L., *Analytical Chemistry*, **24**, 1618 (1952).
- M14** Mellon, M. G., *Analytical Absorption Spectroscopy*. Wiley, New York, 1950.
- M15** Mellon, M. G., *Analytical Chemistry*, **24**, 924 (1952).
- M16** Mellon, M. G., *Quantitative Analysis: Methods of Separation and Measurement*. Crowell, New York, 1955.
- M17** Misra, R. N., and Pani, S., *Journal of the Indian Chemical Society*, **34**, 387 (1957).
- M18** Mitchell, J., Jr., et al. (eds.), *Organic Analysis*, Vol. II. Wiley, New York, 1954.
- M19** Mitchell, J., Jr., WATER, in *Treatise on Analytical Chemistry*, Pt. II, Vol. 1 (I. M. Kolthoff and P. J. Elving, eds.). Wiley, New York, 1961.
- M20** Mitzner, B. M., *Journal of Chemical Education*, **33**, 609 (1956).
- M21** Moore, J. W., and Anderson, R. C., *Journal of the American Chemical Society*, **66**, 1476 (1944).
- M22** Moss, R. L., Pollock, J. McC., and Magee, R. J., *Talanta*, **1**, 184 (1958).
- M23** Muller, R. H., *Analytical Chemistry*, **29**, No. 4, 49A (1957).
- M24** Mysels, K. J., *Journal of Chemical Education*, **32**, 518 (1955).
- M25** Mysels, K. J., *Introduction to Colloid Chemistry*. Wiley, New York, 1959.
- N1** Nicholas, J. D., *Analyst*, **77**, 629 (1952).
- N2** Nielsen, A. E., *Acta Chemica Scandinavica*, **11**, 1512 (1957).
- N3** Nordling, W. D., *Chemist-Analyst*, **51**, 14 (1962).
- O1** Owens-Illinois Glass Co., *The Care and Handling of Glass Volumetric Apparatus*. Toledo, Ohio, 1951.
- P1** Park, B., *Industrial and Engineering Chemistry, Analytical Edition*, **3**, 77 (1931).
- P2** Park, B., *Industrial and Engineering Chemistry, Analytical Edition*, **8**, 32 (1936).
- P3** Pauling, L., *General Chemistry*, 2d ed. Freeman, San Francisco, 1953.
- P4** Phillips, J. P., *Journal of Chemical Education*, **35**, 35 (1958).
- P5** Phillips, J. P., *Automatic Titrators*. Academic Press, New York, 1959.
- P6** Pillion, E., Rogers, M. R., and Kaplan, A. M., *Analytical Chemistry*, **33**, 1715 (1961).
- P7** Pokras, L., *Journal of Chemical Education*, **33**, 152, 223, 282 (1956).
- P8** Pople, J. A., Schneider, W. G., and Bernstein, H. J., *High Resolution Nuclear Magnetic Resonance*. McGraw-Hill, New York, 1959.
- P9** Prideaux, E. B. R., and Ward, A. T., *Journal of the Chemical Society (London)*, **125**, 426 (1924).
- R1** Rao, B. K. S., and Laddha, G. S., *Zeitschrift für analytische Chemie*, **174**, 324 (1960).
- R2** Rehak, B., and Korbl, J., *Collection of Czechoslovak Chemical Communications*, **25**, 797 (1960).
- R3** Rehm, C., and Higuchi, T., *Analytical Chemistry*, **29**, 367 (1957).
- R4** Reilley, C. N., and Crawford, C. M., *Analytical Chemistry*, **27**, 716 (1955).

- R5 Reilley, C. N., and Hildebrand, G. P., *Analytical Chemistry*, **31**, 1762 (1959).
- R6 Reilley, C. N., Schmid, R. W., and Sadek, F. S., *Journal of Chemical Education*, **36**, 555, 619 (1959).
- R7 Reilley, C. N., and Scribner, W. G., *Analytical Chemistry*, **27**, 1210 (1955).
- R8 Ricci, J. E., and Linke, W. F., *Journal of the American Chemical Society*, **73**, 3601 (1951).
- R9 Rieman, W., and Hagen, G., *Industrial and Engineering Chemistry, Analytical Edition*, **14**, 150 (1942).
- R10 Rieman, W., Neuss, J. D., and Naiman, B., *Quantitative Analysis: A Theoretical Approach*, 3d ed. McGraw-Hill, New York, 1951.
- R11 Ringbom, A., *Journal of Chemical Education*, **35**, 282 (1958).
- R12 Robertson, A. J. B., Fabian, D. J., Crocker, A. J., and Dewing, J., *Laboratory Glass Working for Scientists*. Butterworths, London, 1957.
- R13 Rosin, J., *Reagent Chemicals and Standards*, 4th ed. Van Nostrand, New York, 1961.
- R14 Ross, J. W., and Shain, I., *Analytical Chemistry*, **28**, 548 (1956).
- R15 Rossotti, F. J. C., and Rossotti, H., *The Determination of Stability Constants*. McGraw-Hill, New York, 1961.

- S1 Samuelson, O., *Ion Exchangers in Analytical Chemistry*, 2d ed. Wiley, New York, 1962.
- S2 Sandell, E. B., *Colorimetric Determination of Traces of Metals*, 3d ed. Wiley, New York, 1959.
- S3 Schleicher and Schuell Co., *American Filter Papers*. Catalog No. 70. New York, 1949.
- S4 Schmid, R. W., *Chemist-Analyst*, **51**, 56, 60 (1962).
- S5 Schulek, E., Burger, K., and Laszlovszky, J., *Talanta*, **7**, 51 (1960).
- S6 Schwarzenbach, G., *Analyst*, **80**, 713 (1955).
- S7 Schwarzenbach, G., *Analytical Chemistry*, **32**, 6 (1960).
- S8 Scott, A. F., *Analytical Chemistry*, **33**, 23A (August, 1961).
- S9 Scott, W. W., *Standard Methods of Chemical Analysis*, 5th ed. (N. H. Furman, ed.). Van Nostrand, New York, 1939.
- S10 Seidell, A., *Solubilities of Inorganic and Metal Organic Compounds*, 4th ed. (W. F. Linke, ed.). Van Nostrand, New York, 1958.
- S11 Shapiro, L., and Brannock, W. W., *Analytical Chemistry*, **27**, 1796 (1955).
- S12 Shaw, W. H. R., and Lowrance, B. R., *Analytical Chemistry*, **28**, 1164 (1956).
- S13 Sherrill, M. S., King, C. B., and Spooner, R. C., *Journal of the American Chemical Society*, **65**, 170 (1943).
- S14 Siggia, S., *Quantitative Organic Analysis via Functional Groups*, 2d ed. Wiley, New York, 1954.
- S15 Silverman, L., *Chemist-Analyst*, **33**, 8 (1944).
- S16 Skeggs, L. T., *Annals of the New York Academy of Sciences*, **87**, 650 (1960).
- S17 Smith, G. F., *Perchloric Acid*, 4th ed. G. F. Smith Chemical Co., Columbus, Ohio, 1940.
- S18 Smith, G. F., *Cerate Oxidimetry*. G. F. Smith Chemical Co., Columbus, Ohio, 1942.

- S19 Smith, G. F., *Mixed Perchloric, Sulfuric, and Phosphoric Acids and Their Applications in Analysis*, 2d ed. G. F. Smith Chemical Co., Columbus, Ohio, 1942.
- S20 Smith, G. F., *Dehydration Studies*. G. F. Smith Chemical Co., Columbus, Ohio, 1943.
- S21 Smith, G. F., *Periodic Acid and Iodic Acid*, 5th ed. G. F. Smith Chemical Co., Columbus, Ohio, 1950.
- S22 Snelling, W. O., *Journal of the American Chemical Society*, **31**, 456 (1909).
- S23 The Society for Analytical Chemistry, Analytical Methods Committee, *Analyst*, **84**, 214 (1959).
- S23a Someya, K., *Zeitschrift für anorganische und allgemeine Chemie*, **169**, 293 (1928).
- S24 Sorum, C. H., *How to Solve General Chemistry Problems*, 2d ed. Prentice-Hall, Englewood Cliffs, N.J., 1958.
- S25 Souchay, P., and Lourijsen, M., *Bulletin de la Societe chimique de France*, 893 (1956).
- S26 Stacey, I. F., *Journal of Chemical Education*, **32**, 90 (1955).
- S27 Steinbach, J., and Freiser, H., *Analytical Chemistry*, **24**, 1027 (1952).
- S28 Stern, M., Shwachman, H., Licht, T. S., and deBethune, A. J., *Analytical Chemistry*, **30**, 1506 (1958).
- S29 Stott, V., *Journal of the Society of Glass Technology*, **5**, 307 (1921); **7**, 169 (1923).
- S30 Streuli, C. A., *Analytical Chemistry*, **34**, 302R (1962).
- S31 Strobel, H. A., *Chemical Instrumentation*. Addison-Wesley, Reading, Mass., 1960.
- S32 Suk, V., and Malat, M., *Chemist-Analyst*, **45**, 30 (1956).
- S33 Sweetser, P. B., and Bricker, C. E., *Analytical Chemistry*, **25**, 253 (1953).
- S34 Swett, O. D., *Journal of the American Chemical Society*, **31**, 928 (1909).
- S35 Swift, E. H., *A System of Chemical Analysis for the Common Elements*. Freeman, San Francisco, 1939 (reissued 1955).
- S36 Swift, E. H., *Introductory Quantitative Analysis*. Prentice-Hall, Englewood Cliffs, N.J., 1950.
- S37 Swift, E. H., Arcand, G. M., Lutwack, R., and Meier, D. J., *Analytical Chemistry*, **22**, 306 (1950).
- T1 Theobald, L. S., *Analyst*, **84**, 570 (1959).
- T2 Treadwell, F. P., and Hall, W. T., *Analytical Chemistry*, 9th ed. Wiley, New York, 1937-42. 2 vols.
- U1 Udenfriend, S., *Fluorescence Assay in Biology and Medicine*. Academic Press, New York, 1962.
- U2 Underwood, A. L., *Journal of Chemical Education*, **31**, 394 (1954).
- U3 U.S. National Bureau of Standards, PRECISION LABORATORY STANDARDS OF MASS AND LABORATORY WEIGHTS. Circular 547. Washington, D.C., 1954.
- U4 U.S. National Bureau of Standards, STANDARD SAMPLES AND REFERENCE STANDARDS ISSUED BY THE NATIONAL BUREAU OF STANDARDS. Supplement to Circular 552. Washington, D.C., 1954.
- U5 U.S. National Bureau of Standards, CERTIFICATE FOR STANDARD SAMPLE 185b, POTASSIUM HYDROGEN PHTHALATE (pH STANDARD). Washington, D.C., 1955.

- U6 U.S. National Bureau of Standards, *TESTING OF GLASS VOLUMETRIC APPARATUS*. Circular 602. Washington, D.C., 1959.
- U7 U.S. National Research Council, *International Critical Tables of Numerical Data*. McGraw-Hill, New York, 1926-33. 7 vols.
- U8 U.S. Pharmacopoeial Convention, *Pharmacopoeia of the United States of America*, 16th Revision. Mack Publishing Co., Easton, Pa., 1960.
- U9 Unterzaucher, J., *Analyst*, **77**, 584 (1952).

- V1 Van Hook, A., *Crystallization: Theory and Practice*. (American Chemical Society Monograph No. 152.) Reinhold, New York, 1961.
- V2 Vetter, K. J., and Bardeleben, J., *Zeitschrift für Elektrochemie*, **61**, 135 (1957).
- V3 Viswanathan, A., and Gireesan, S., *Journal of Chemical Education*, **34**, 154 (1957).
- V4 Vogel, A. I., *A Textbook of Quantitative Inorganic Analysis*, 3d ed. Wiley, New York, 1961.
- V5 von Weimarn, P. P., *Die Allgemeinheit des Kolloidzustandes*. Dresden, Steinkopf, 1925.

- W1 Waggoner, W. H., *Journal of Chemical Education*, **35**, 339 (1958).
- W2 Wahl, A. C., and Bonner, N. A., *Radioactivity Applied to Chemistry*. Wiley, New York, 1951.
- W3 Walden, G. H., Hammett, L. P., and Edmonds, S. M., *Journal of the American Chemical Society*, **56**, 350 (1934).
- W4 Walton, G., and Walden, G. H., *Journal of the American Chemical Society*, **68**, 1742, 1750 (1946).
- W5 Walton, H. F., *Principles and Methods of Chemical Analysis*. Prentice-Hall, Englewood Cliffs, N.J., 1952.
- W6 Watts, H. L., *Analytical Chemistry*, **32**, 1189 (1960).
- W7 Watts, H. L., and Utley, D. W., *Analytical Chemistry*, **28**, 1731 (1956).
- W8 Weiser, H. B., *Colloid Chemistry*, 2d ed. Wiley, New York, 1949.
- W9 Welcher, F. J., *Organic Analytical Reagents*. Van Nostrand, New York, 1947-48. 4 vols.
- W10 West, P. W., and Coll, H., *Analytical Chemistry*, **28**, 1834 (1956).
- W11 Whitehead, T. H., *Journal of Chemical Education*, **36**, 297 (1959).
- W12 Whiteker, R. A., and Swift, E. H., *Analytical Chemistry*, **26**, 1602 (1954).
- W13 Wichers, E., Finn, A. N., and Clabaugh, W. S., *Industrial and Engineering Chemistry, Analytical Edition*, **13**, 419 (1941).
- W14 Willard, H. H., Furman, N. H., and Bricker, C. E., *Elements of Quantitative Analysis*, 4th ed. Van Nostrand, New York, 1956.
- W15 Willard, H. H., and Merritt, L. L., *Industrial and Engineering Chemistry, Analytical Edition*, **14**, 486 (1942).
- W16 Willard, H. H., Merritt, L. L., and Dean, J. A., *Instrumental Methods of Analysis*, 3d ed. Van Nostrand, New York, 1958.
- W17 Willits, C. O., *Analytical Chemistry*, **23**, 1058 (1951).

- Y1 Yoe, J. H., *Photometric Chemical Analysis*. Wiley, New York, 1928-29. 2 vols.
- Y2 Yoe, J. H., and Koch, H. J., *Trace Analysis*. Wiley, New York, 1957.
- Y3 Young, P., *Analytical Chemistry*, **24**, 152 (1952).

INDEX

- Absorbance, 512, 514; *see also* Transmittance
- Absorption
 - of CO_2 , 155
 - of light, 506, 508
 - of water, 152-54, 156, 686
- Absorption cells, 517, 530, 868
- Absorption curves, 512, 514, 522, 529, 875
- Absorptivity, 511
- Acceptor
 - in coordination compounds, 559
 - electron, 395
 - in induced reactions, 32, 812
 - proton, 316
- Accuracy; *see also* Deviation; Errors; Precision
 - checking of, 53, 636
 - contrasted with precision, 37
 - effect of, on choice of method, 8
 - sought in analysis, 51
- Acetate
 - as buffer solution, 321-24
 - hydrolysis of, 326
- Acetic acid
 - in BaSO_4 determination, 221
 - as buffer solution, 321-24
 - in Fajans determination of chloride, 297
 - glacial, composition of, 913
 - ionization of, 319
 - titration curves of, 345-49
- Acetone
 - coagulation of colloids by, 722
 - for drying precipitates, 219
- Acid-base equilibria, 29, 316-37, 768-75, 784-93
- Acid-base indicators, 352, 778-83, 914, 928; *see also* name of indicator
- Acid-base ionization theory, 316, 326, 769
- Acid-base titrations; *see also* names of substances or types of titrations
 - carbonate and silicate error in, 358, 371
 - errors in, 355, 783
 - graphical method of Gage, 790
 - with indicators, 352, 778-83
 - with pH meter, 350, 363, 371-78, 778, 785, 792
 - primary standards for, 793
 - of salts, 350, 363, 370, 371, 795-99
 - titration curves, 343-51, 361-65, 369, 375, 781, 784-92
- Acids; *see also* name of acid
 - calculation of pH of, 318-37, 346-48, 364, 769-75, 783, 792
 - composition and density of, 913
 - conjugate, 317
 - determination of, with KIO_3 , 467, 845
 - for dissolution of samples, 113
 - equivalent weight of, 237
 - ionization of, 22, 29, 316, 319, 332, 335, 923, 925; *see also* Equilibrium constants
 - monoprotic, 319
 - polyprotic, 332, 361-65, 370-78, 578, 792, 795-99
 - potentiometric titration of, 350, 371-78
 - primary standard, 366, 793
 - removal of, by evaporation, 133
 - standard solutions of; *see* name of acid
 - strong and weak, lists of, 22, 923, 925
 - titration of, 343-85
- Acrylonitrile, chain suppressor, 816
- Activated complex, 810
- Activity coefficients, 701, 921
- Activity effects
 - in acid-base equilibria, 775
 - on cell voltage, 446, 808
 - in chemical equilibria, 28, 171, 446
 - in redox equilibria, 808
 - in solubility equilibria, 701, 708, 711
- Activity equilibrium constants, 701
- Adsorbate, 187, 682
- Adsorbed-ion layer, 186
- Adsorbent, 187, 682
- Adsorption
 - chemical vs. physical, 683-85

- Adsorption—*Cont.*
 and coprecipitation, 201
 effect of, on titration curve, 276, 764
 (Prob. 1)
 of lead ion on CaSO_4 , 191
 by precipitates, 185–93, 201, 719
 by surface exchange, 707
 of water vapor, 151, 682–85
- Adsorption indicators, 286–89, 295, 756, 763
- Adsorption isotherm, 189, 684, 698
 (Prob. S20)
- Aging of precipitates, 183, 189, 203, 704, 727
- Air
 analysis of
 for CO_2 , 155, 805 (Prob. S8)
 for oxygen, 856–57
 for ozone, 467
 for water, 155, 689
 density of, 659
 drying by, 103, 153, 682, 686
 drying of, 686
 exclusion of, from standard
 solutions, 98, 360, 855
- Air bath, 102, 133
- Air buoyancy in weighing, 49, 83, 658, 751
- Alcohol
 coagulation of colloids by, 722
 for drying precipitates, 219
- Alcohols, titration of, 837, 846, 852
- Aldehydes, titration of, 467, 759, 837, 846, 852
- Aliquot techniques, 235, 269
- Alkalies; *see* Bases; *name of element*
- Allotropism, and solubility, 704, 711
- Alloys; *see name of alloy*
- Alumina
 as desiccant, 687
 drying of, 47
 in rocks and ores, 477, 481, 488
 solubility of, 164
- Aluminum
 gravimetric determination of, 47, 212, 570
 as reducing agent, 379, 489
 volumetric determination of, 230, 471, 584, 790, 854
- Aluminum ion
 complexing of, by oxalate, 482
 hydrolysis of, 769
- Aluminum oxide, hydrous
 contamination of, 47, 201
 gelatinous nature of, 184
 solubility of, 709, 769
 as a weighing form, 212
- Amalgams, as prereductants, 820
- Amines, titration of, 837, 846, 852
- Amino acids
 ionization of, 336
 titration of, 789
- Ammonia
 as complexer for metals, 296, 520, 561, 566–67, 573–75
 composition of reagent, 913
 Haber process for, 31
 ionization of, 320
 Kjeldahl determination of, 378
 purification of, by distillation, 47
 spectrophotometric determination of
 Cu with, 520
 titration curves of, 349, 573–75
 volumetric determination of, 378
- Ammonium salts, evaporation of, 133, 692
- Ammonium sulfate, primary standard, 799
- Amperometric titrations, 543
- Amphiprotic substances, 317, 335
- Amphoteric substances, 317, 335
- Amplitude of balance swings, 655
- Analysis; *see also name of element, material, or method*
 details of an, 68
 importance of, 2
 indirect; *see* Indirect analysis
 of mixtures; *see* Mixtures
 types of, 6–8
- Analytical methods; *see also name of element or method*
 checking accuracy of, 4, 53, 636
 choice of, 7
 classification of, 6–8, 10–13, 231, 537–40
 errors inherent in, 48
 list of, 539
- Analytical process, general outline of, 7
- Analytical result, report of, 41, 144, 146
- Ångstrom unit, 506
- Anhydrous, as desiccant, 155, 687
- Annealing of glass, 135
- Antimony
 gravimetric determination of, 212, 570
 interference of, in Cu determinations, 489
 preoxidation and prereduction of, 488, 819, 822
 volumetric determination of, 456, 467, 471, 844, 853
- Apparatus; *see also function or name community*, 64, 139
 locker, 910
- Approximations, 17, 562, 610, 643, 770
- Argent ion, 818
- Argentimetric titrations; *see* Precipitation titrations
- Arithmetic mean; *see* Mean

- Arsenic**
interference of, in Cu determination, 489
preoxidation and prereduction of, 488, 819, 822
volumetric determination of, 302, 456, 467, 471, 844, 849, 853, 857
- Arsenious oxide**, primary standard, 439, 454, 461, 469, 853
- Arsenite**
reaction of, with iodine, 461, 849
reaction with cerate, 469
reduction of H_2O_2 with, 844
standard solution of, 439, 456, 847
- Asbestos mat** for Gooch crucible, 125
- Asbestos suspension**, preparation of, 915
- Ascarite**, 155
- Ash content** of filter paper, 118
- Ashing**, dry or wet, 735, 818–20
- As-received basis**, analysis on, 146
- Asymmetry potential**, 554, 829
- Automatic control** of processes, 547
- Automatic titrations**, 544, 778, 832
- Average**; *see* Mean
- Average deviation**; *see* Deviation
- Azeotropic solutions**, as primary standards, 795
- Azo compounds**, titrations of, 856–57
- Back titration**, 230, 241, 260, 301, 456, 467, 471, 474, 475, 589, 591, 837, 844, 852, 854; *see also* name of method
- Baking of precipitates**, 132, 739
- Balance**, analytical, 70–91, 649–66
arm ratio of, 82, 91
chain, 84, 90; *see also* Weights
maintenance and repair of, 87, 665
parts and construction of, 73
period of, 653
rest point of, 76–79, 88, 655–57
sensitivity of, 71, 88, 650, 661
sources of error in use of, 79–84; *see also* Weighing, errors in
theory of, 70, 649–53, 655
types of, 84, 660
weighing with, 76–79, 87–91; *see also* Weighing
- Balance**, specific gravity, 669 (Prob. S11)
- Balancing redox equations**, 398
- Barium**
gravimetric determination of, 212, 737, 740
homogeneous precipitation of, 740
volumetric determination of, 456, 467, 584
- Barium chloride**
determination of water in, 156
primary standard, 694
reagent solution, 913
sample series of, with NaCl, 694
- Barium hydroxide**, as carbonate-free standard base, 359
- Barium oxide**, as desiccant, 687
- Barium sulfate**; *see also* Sulfate
contamination of, 201, 206, 224
crystallization of, 183, 728
drying of, 223
gum arabic for stabilization of, 882–85
precipitation of, 184, 201, 221, 727
reduction of, by carbon, 223
solubility of, 162, 172, 223
supersolubility of, 727
- Bases**; *see also* Acid-base entries; name of base
calculation of pH of, 316–37, 346–48, 364, 769–75, 783, 792
carbonate or silicate in, 358, 365, 371, 376
composition and density of solutions of, 913
conjugate, 317
equivalent weight of, 237
ionization and ionization constants of, 22, 29, 316, 320, 335, 923, 925; *see also* Equilibrium constants
monoequivalent, 320, 335
polyequivalent, 331–37, 795–99
potentiometric titration of, 350, 784–92
primary standard, 366, 793
standard solutions of; *see* name of solute
titration of, 343–85
- Basic salts**, 769
- Becker-Doering nucleation equation**, 716
- Beer's law**, 511–22, 869–75
- Benzene**, for cleaning glassware, 250
- Benzoic acid**, primary standard, 793
- Beryllium**
fluorimetric determination of, 886
gravimetric determination of, 212
- Bicarbonate**
determination of, in carbonate or hydroxide mixtures, 795
titration curve of, 362, 369
- Bismuth**
gravimetric determination of, 212, 570
as prereducer, 820
volumetric determination of, 456, 584, 587, 590, 857
- Bismuth sulfide**, postprecipitation of ZnS on, 198
- Bismuthate**, as preoxidant, 441, 819, 822
- Blank**
in acid-base titrations, 357
in Fajans titration, 295
indicator, 357

- Blank—*Cont.*
 in Mohr titration, 304
 in permanganimetric titrations, 457
 for reducing constant errors, 49
 in spectrophotometry, 519
 in Volhard titration, 285, 300, 303, 766 (Prob. S11)
- Blood, as a buffer, 325
- Boiling chips, 132
- Borate, titration of, 350, 380, 788
- Borax
 as preservative for $\text{Na}_2\text{S}_2\text{O}_3$, 464, 490
 primary standard, 793
- Boric acid
 as absorbent for NH_3 , 380
 titration of, 345, 784–92
- Bottles
 plastic, 98, 123, 138, 359, 557, 592, 839
 reagent, 98, 360
 safety, for aspirator, 127
 wash, 138
 weighing, 111
- Brass, determination of Cu in, 490
- Bridge, for electrochemical cell, 415, 418, 447, 896
- Bromate
 gravimetric determination of, 735
 titrations with, 451, 853
 volumetric determination of, 467
- Bromide; *see also* Bromine
 as chain suppressor, 815
 as complexer for Hg, Pd, Au, Cu, 571–72
 gravimetric determination of, 735
 volumetric determination of, 302, 572, 763, 844
- Bromine; *see also* Bromide
 determination of, in organic compounds, 735
 oxidation of Fe(II) with, 485, 591
 volumetric determination of, 467, 854
- Bromocresol green, 366, 383, 914, 928
- Bromocresol green–methyl red, 336, 782
- Brönsted's theory, 316, 326, 769
- Buffer solutions, 321, 768
 of potassium acid phthalate, 915
- Bumping, 102, 132
- Bunsen valve, 360
- Buoyancy weighing error, 49, 83, 658
- Burets; *see also* Volumetric apparatus
 calibration of, 263, 268, 751
 cleaning of, 248
 drainage from, 259, 746
 greasing stopcocks of, 252
 precision of, 247, 748
 reading of, 255
 specifications and tolerances of, 748
 types of, 247
 use of, 258, 746
- Burners, types of gas, 100
- Cadmium
 gravimetric determination of, 212, 570
 as prereducer, 820
 volumetric determination of, 467, 584, 844
- Calcite; *see* Calcium carbonate
- Calcium, determination of, 212; *see also name of compound*
- Calcium carbonate
 decomposition of, 690
 determination of, in limestone, 481
 gravimetric determination of, 212, 481, 737
 primary standard, 793
 volumetric determination of, 231, 241, 456, 471, 481
- Calcium chloride, as desiccant, 686
- Calcium hydroxide, decomposition of, 676
- Calcium oxalate
 coprecipitation by, 197, 481
 direct titration with EDTA, 582, 584, 587, 589, 590–94
- Calcium oxide
 as desiccant, 686
 determination of, in limestone, 481, 590
 as weighing form for Ca, 212
- Calcium sulfate
 adsorption of lead ion by, 191
 as desiccant, 686
 solubility of, 737
 as weighing form for Ca, 212
- Calcon; *see* Eriochrome Black
- Calculations; *see also* Approximations;
name of topic
 error of a computed result, 14, 57, 640
 gravimetric, 11, 140–46
 with logs, 165, 901
 the mole concept in, 140, 236
 precision of, 14, 54–58, 639–44
 in solving algebraic equations, 15–18, 610
 standard deviation of a calculated result in, 640
 volumetric, 11, 235–42, 401
- Calibration; *see also* Working curves
 of absorption cells, 530
 of potentiometer, 419
 of volumetric apparatus, 263–69, 751;
see also name of apparatus
 of weights, 83, 89, 90, 657; *see also*
 Weights
- Calibration correction, 49, 90, 263–69, 657
- Calomel electrode, 418
- Capillary leak, for bumping, 132
- Carbon, determination of, 155, 212
- Carbon dioxide; *see also* Carbonate
 in air, 155, 690

- automated determination, 547
- in limestone, 155, 481
- Carbon dioxide error, in acid-base titrations, 358, 365, 371, 376
- Carbon tetrachloride, for iodine end point, 459
- Carbonate; *see also* Carbon dioxide
 - gravimetric determination of, 155, 212, 690
 - mixtures, *pH* of, 333–35
 - titration of, in hydroxide or bicarbonate mixtures, 795
 - titration curves of, 362, 369
- Carbonate error, in acid-base titrations, 358, 365, 371, 376
- Carbonate-free standard base, 359
- Carius oxidation, 736
- Carrying, of traces by adsorption, 191
- Catalysis, 31, 812
 - of air-oxidation of iodide, 462
 - of arsenite-cerate reaction, 469, 851
 - of arsenite-permanganate reaction, 455
 - of chromous chloride decomposition, 857
 - of formate-permanganate reaction, 837
 - of oxalate-permanganate reaction, 839
 - of titration reactions, 230
- Cells; *see* Electrochemical cells
- Cellulose ester filters, 118
- Cerate titrations, 468, 478
 - determination of organic compounds by, 852
- Ceric salts, 468
- Cerium
 - precipitation with oxine, 570
 - preoxidation of, 818–24
 - volumetric determination of, 456, 467, 589, 855–57
- Chain balance, 84, 90; *see also* Weights
- Charge on colloids, 186, 190–92, 707, 719–22
- Chelate compounds, 565–69
- Chemical equations
 - interpretation of, 21
 - ionic, 23
 - redox, 395, 398
 - types of, 28, 230
- Chemical equilibria; *see also specific types*
 - Brönsted concepts of, 316, 326, 769
 - effect of, on light absorption, 873
 - elementary discussion of, 23–29
 - equilibrium constants from electrochemical data, 421
 - independent, 770
 - multiple, 327, 561–63, 769–75
 - and reaction rate, 30, 424, 809–17
 - solid-gas, 676–85, 691, 698 (Prob. S11), 700 (Prob. S4)
- Chemical equilibrium, principal, 328
- Chemicals; *see* Reagents
- Chlorate
 - determination of, as AgCl, 735
 - as preoxidizer, 822
 - volumetric determination of, 467, 844, 856, 857
- Chloride; *see also* Chlorine
 - argentimetric titrations of, 273–308, 758, 760
 - as complexer for Fe(III), 842
 - determination of, in organic compounds, 302, 735, 759
 - effect of, on AgCl solubility, 734
 - gravimetric determination of, 204, 212, 214, 671
 - mercurimetric titration of, 572
 - oxidation of, by permanganate, 841
 - potentiometric determination of, 550, 895
 - removal of, by evaporation, 133
- Chlorine; *see also* Chloride
 - determination of, in organic compounds, 302, 735, 759
 - iodimetric determination of, 467
- Chlorite, determination of, as AgCl, 735
- Chloroform, for iodimetric end point, 459
- Christiansen-Nielsen nucleation equation, 716
- Chromate; *see also* Chromium
 - as indicator for Mohr titration, 281, 303, 754
- Chromium
 - determination of, in ores and steel, 474
 - interference of, with Fe determination, 477
 - interference of, in spectrophotometric permanganate determination, 529
 - precipitation with oxine, 570
 - preoxidation and prereduction of, 474, 818–24
 - spectrophotometric determination of, in presence of Mn, 530
 - volumetric determination of, 456, 471, 472, 584
- Chromous chloride titrations, 452, 857
- Chronopotentiometric titrations, 543
- Citrate, as complexer, 225
- Classical methods of measurement, 10, 538
- Cleaning
 - of filter crucibles, 128
 - of volumetric glassware, 248
- Cleaning solutions, 248
- Clear point, in titration, 281
- Cobalt
 - gravimetric determination of, 212, 570
 - preoxidation of, 822
 - volumetric determination of, 584, 844
- Colloidal precipitates, 184

- Colloids
 adsorption by, 185-93
 coagulation of, 185, 193, 295, 720
 description of, 184
 dialysis of, 194
 hydrophilic, 184, 193, 722
 hydrophobic, 184, 193, 720
 peptization of, 185, 194, 219, 721
 stabilization of, 193, 295, 721, 883, 885
- Color, 507
 of indicators, 352, 447, 585, 756, 778, 833
- Color development, in spectrophotometry, 509, 523, 542, 570, 588
- Colorimetry, 525, 888; *see also* Spectrophotometry
- Columbium, gravimetric determination of, 212
- Common-ion effect, 25, 163, 167
- Community equipment, use of, 64, 139
- Comparison solutions, 378, 492, 530
- Completeness of precipitation, 116, 161, 169
- Complexation constants; *see* Equilibrium constants
- Complexers; *see also name of substance*
 as color formers in spectrophotometry, 523, 570, 587
 effect of, on cell voltage, 446
 effect of, on E , 408, 424
 effect of, on equilibrium, 25
 as indicators, 284, 585, 836, 856
 in titrations, 559-94, 788
- Computations; *see* Calculations
- Concentration, effect of
 on chemical equilibrium, 25
 on E , 406
 on reaction rate, 31
 on titration curves, 275, 349
- Concentrations
 effect of temperature on, 264, 751
 expression of, 21, 235, 401, 406, 409
 range of standard solution, 233
 reagent, 913-15
- Conductometric titrations, 289, 543
- Confidence levels
 for mean, 618, 621
 for standard deviation, 615, 628
- Conjugate pairs, 317, 396
- Constant boiling acids, primary standard, 795
- Constant weight, achievement of, 112
- Containers, 98, 111, 360
 marking of, 133, 749
 weighing, handling of, 111
- Contamination, testing reagents for, 117
- Contamination of precipitates
 during analysis, 211
 prevention of, by buffering, 325, 483
 sign of contamination error in, 206
- types and reduction of, 195-206, 719, 723-28
- Control determination, for reducing errors, 50, 238, 636
- Control work, 545
- Conversion
 in indirect analysis, 671
 of sought-for substance to measurable form, 10
- Conversion factors, 143, 244 (Prob.19)
- Cooling
 of glassware, 128, 135
 of objects for weighing, 80, 107
- Coordination compounds, 559-69
 with EDTA, 574-94
 stability of, 561, 576
- Copper
 as catalyst for air-oxidation of KI, 462
 determination of, in brass, 490
 determination of, in ores, 488
 gravimetric determination of, 212, 570
 as prereducer, 822
 primary standard, 440, 464, 491, 857
 separation of, from interferences, by deposition on Al, 489
 spectrophotometric determination of, 520, 525, 571, 893 (Prob. S3)
 spectrophotometric titration of, 542, 587
 volumetric determination of, 456, 467, 471, 488, 582, 584, 844, 856, 857
- Copper ores; *see* Copper
- Copper-silver alloy; *see* Silver-copper alloy
- Coprecipitation
 in argentimetric titrations, 289, 297, 763
 in determination of AgCl, 220
 in determination of BaSO₄, 224
 types of, 195
- Corrections, 49; *see also* Blank;
 Calibration correction; Control determination
 for buoyancy on weight, 49, 83, 263, 658
 by compensation procedures, 51
 for effect of temperature on concentration, 264
 limitations on use of, 48, 51, 636
- Coulometric titrations, 543
- Counter-ion layer, 187
- Counterpoise, 81, 82, 267, 660, 670
- Creeping, 132
- Crucibles, types, properties, and use of, 103-6, 115, 125-29, 131, 133, 215
- Crystalline precipitates, 179-84, 717
- Crystals, formation of, 178-84, 704, 716-19
- Cupric nitrate, pyrolysis of, with thermobalance, 692

- Cupric sulfate, vapor pressure of hydrates, 698 (Prob. S11)
- Cuprous iodide, solubility of, in KI, 490
- Cyanide
determination of, 302, 572, 837
masking by, 570, 591
- Cylinders, graduated, 245
- Damped oscillations, of balance, 655
- Damping of balances, 665
- Data
discordant, 67, 632
recording of, 67
summary, pages of, 67, 157, 216, 294, 367
- Decantation, 120
- Decomposition, of samples, 9, 113
- Decomposition methods of analysis, 150-57, 690-94
- Decomposition pressure, 677
- Degree of supersaturation, 179-83, 716
- Dehydrating agents; *see* Desiccants
- Density
of air, 659
in analyzing two-component systems, 538
of metals used in weights, 659
of reagents, 911
- Desiccants, 686
- Desiccators, 106, 686
- Desorption, 190, 202
- Determinate error; *see* Errors
- Determinations; *see name of element or compound*
- Devarda's alloy, reduction of nitrate with, 379, 821
- Deviation, 38, 44, 615; *see also* Accuracy; Errors; Precision; Standard deviation
- Dew point, 689
- Dextrin, 194, 295
- Dialysis, 194
- Dichlorofluorescein, 286, 295, 756, 914
- Dichromate
absorption curve of, 529
in cleaning solution, 248
spectrophotometric determination of, 530
titrations with, 472, 476
volumetric determination of, 456, 467, 844, 856, 857
- Didymium glass, 512
- Digestion, 117, 203, 728
in Kjeldahl method, 379
- Diketones, volumetric determination of, 856, 857
- Dilution to volume, 262
- Dimethyldiiodofluorescein, 758, 763
- Dimethylglyoxime, in Ni determination, 213
- Diphenylamine sulfonic acid, 448, 472, 479, 835, 914
- Diphenylcarbazone, 571
- Disk, perforated, for Gooch crucible, 126
- Dissociation constants; *see* Equilibrium constants
- Dissolution of samples, 9, 113, 205, 476, 481, 488
- Distillation; *see also* Evaporation; Volatilization
determination of NH_3 by, 378
determination of water by, 688
of HCl solutions, 795
preventing entrainment in, 382
purification of NH_3 reagent by, 47
purification of water by, 99
of sulfuric acid solutions, 795
- Distilled water, 99, 117, 215, 221, 365, 519
- Distribution
of mean, \bar{X} , 618
of measurements, 613-15
of standard deviation, s, 615
- Distribution curve, 43, 613
- Dithizone, for spectrophotometric determinations, 525, 571
- Donors; *see* Acceptors
- Double salts, formation of, 723
- Double weighing, 83, 91, 657
- Drainage from burets and pipets, 746
- Drop size, effect on vapor pressure, 706
- Droppers, glass, 138
- Dry ashing, 735, 820
- Dry basis, analysis on, 9, 146
- Drying, 9, 103-9, 112, 153, 211, 212, 219, 223, 686
- Drying agents, 686
- Duboseq colorimeter, 888
- Dumas determination of N, 381
- EDTA; *see* Ethylenediaminetetraacetic acid
- Electric heat sources, 100
- Electrical properties, analytically useful, 540
- Electrification, as source of weighing error, 80
- Electrochemical cells, 413
amount of electricity from, 420
for measurement of equilibrium constants, 421
voltage of, 416-19, 445, 827-33
- Electrode potentials; *see* Single-electrode potentials
- Electrodeposition, elements determined by, 212
- Electrodes
Ag-AgCl, 895-98
calomel, 418, 447
glass, 828

- Electrodes—*Cont.*
 Hg-HgY=, 582
 indicator, 445, 827
 miscellaneous types, 418, 827, 830, 831
 rate of response of, 828, 830
 reference, 445, 832
 true voltage of, 415
- Electrolytes
 coagulation of colloids by, 194, 295, 720
 solubility and ionization of, 22–24, 26–29
- Electromagnetic balance, 665
- Electromagnetic energy, 505
- Emission spectroscopy, 13, 539
- Empirical methods of analysis, 144, 510, 539
- End point; *see also name of method or standard solution*
 in acid-base titrations, 350–55
 definition of, 280
E at, 441–45, 582–88, 824
 in EDTA titrations, 582–88
 by instrumental methods, 540–44
 in precipitation titrations, 279–89, 754
 in redox titrations, 445–52
- End-point errors; *see name of method*
- Energy, radiant or electromagnetic, 505
- Entrainment in distillation, 382
- Eosin, 295, 758
- Equal turbidity, method of, 281
- Equations
 algebraic, solving, 15, 610
 chemical; *see* Chemical equations
- Equilibria; *see* Chemical equilibria;
name of type
- Equilibrium constants; *see also name of type*
 from electrochemical cell data, 421
 tables of, 916, 923, 925, 932
- Equipment; *see also name or function*
 community, 64, 139
 locker, 910
- Equivalence point; *see* End point
- Equivalent weight, 237, 401
- Eriochrome Black, 585, 590–93
- Error curve, 43, 613, 908, 909
- Errors, 38; *see also* Accuracy; Deviation;
 Precision; *names of determinations, techniques, or kinds of error*
 computational; *see* Calculations
 determinate, 45
 compensation of, 51, 636, 638, 741;
see also Proportional error
 discovery of, 45, 636
 kinds of, 46
 reduction of, 46; *see also* Blank;
 Calibration correction; Control
 determination; Corrections
 gross, 53, 633
 made by students, 634
 maximum, 57
 proportional; *see* Proportional error
 purposes of study of, 41
 random, 41–45, 80, 613–35
 sources of, 48
 weighing, 81
- Ethanol, determination of water in, 688, 689
- Ethylenediaminetetraacetic acid, 224, 225, 542, 574–94
- Evaporation, 130–33
- Evolution
 of carbon dioxide, 155, 690
 of gases, 115, 150–57, 676–94
 of water, 152–57, 676–88
- Evolution methods of analysis, 150–57, 690–94
- Exchange adsorption, 707
- Expansion
 of solutions, 264
 of volumetric glassware, 264
- Experimental work; *see* Students, work of
- Exponents, 15, 901
- External indicator, 283, 451
- Extraction of samples, 9, 113
- Eye, sensitivity of, 869
- F test, 629
- Factor
 gravimetric, 143
 volumetric, 244 (Prob. 19)
- Factor weights of sample, 670
- Fajans titration for chloride, 287, 295
- Fatty acids, determination of, 526
- Feedback loop, 545
- Ferric ion; *see also* Ferrous ion; Iron
 absorption spectrum of, 529
 complexing of, 225, 482, 528, 842
 hydrolysis of, 769
 as indicator, 284, 298–303, 572
 precipitation with oxine, 570
 spectrophotometric titration, 587–88
 thiocyanate indicator for, 856
 volumetric determination of, 467, 582, 590, 856
- Ferric nitrate, reagent solution of, 913
- Ferric oxide, hydrous
 contamination of, 192
 gelatinous nature of, 184
 weighing form of, 212
- Ferric sulfate, behavior of, on heating, 692
- Ferricyanide
 as indicator for Fe(II), 451
 standardization of $\text{Na}_2\text{S}_2\text{O}_3$ with, 850
 volumetric determination of, 467
- Ferrocyanide
 for determination of zinc, 283, 290

- volumetric determination of, 456, 467, 471, 853
- Ferrioin, 448, 469, 472, 479, 836, 914
- Ferrous ammonium sulfate, 440, 476
- Ferrous ion; *see also* Ferric ion; Ferrous sulfate; Iron
 - ferricyanide as indicator for, 451
 - oxidation of, by bromine, 485, 591
 - reaction with peroxide, 814
 - as reductant, 735
 - volumetric determination of, 841, 844, 853
- Ferrous sulfate
 - primary standard, 440
 - standard solution of, 456, 471, 474, 475
- Filter
 - cellulose ester, 118
 - fluted, 120
- Filter crucibles, 106, 125–29
- Filter disks, glass-fiber, 126
- Filter flasks, 127
- Filter papers, 104, 118–25, 129
- Filter photometer, 522
- Filter pulp, 119
- Filtrate, testing, 124, 128
- Filtration, 117–30, 184
- Fixation of nitrogen, 30
- Flasks
 - filter, 127
 - volumetric; *see also* Volumetric apparatus
 - calibration of, 263, 267, 269, 751
 - cleaning of, 248
 - precision of, 248, 746
 - reading of, 255
 - specifications and tolerances for, 746
 - use of, 257, 748
- Fluorescein, 286, 295, 756
- Fluorescence, 506, 525, 782, 885
- Fluorescent indicators, 355, 782
- Fluoride
 - as complexer for metal ions, 489, 789
 - gravimetric determination of, 723
 - spectrophotometric determination of, 523
 - volumetric determination of, 290, 759
- Fluorimetric determinations, 525, 885
- Fluxes, 115, 474, 481, 818
- Formal concentration, 409
- Formal potentials; *see* Single-electrode potentials
- Formaldehyde
 - in amino acid titration, 789
 - in ammonia determination, 381
 - interference of, in AgCl determination, 220
 - volumetric determination of, 759, 837, 852
- Formic acid, volumetric determination of, 456, 837, 852
- Formulae, chemical, interpretation of, 21
- Freundlich equation, 189, 698 (Prob. S20)
- Fuming with acids, 133, 488, 691
- Funnels, types and use of, 112, 115, 117–25
- Furnace, electric, 101
- Fusions, 9, 115, 474, 476, 482, 487, 818
- Gallium
 - EDTA titration, 584
 - oxine precipitation, 570
- Gas equilibria
 - of carbon dioxide, 690
 - of hydrates, 678–88
 - miscellaneous, 406, 676–88, 690–94
- Gas titrations, 543
- Gases, determination of water in, 689
- Gasometric method of analysis, 12
- Gaussian distribution curve, 43, 613–20
- Gelatinous precipitates, filtration of, 119, 184
- Gels, 193, 722
- Glass electrodes, 828
- Glass-fiber filter disks, 126
- Glass hooks, 100, 115, 136
- Glassware
 - attack during evaporation, 130
 - attack by reagents, 98, 130, 358
 - cleaning of, 248
- Glassworking, 134
- Glucose, oxidation of, 31
- Glycerol, determination of, with cerate, 852
- Glycine, ionization of, 336
- Glycols, determination of, 846, 852
- Gold, complexation by dithizone, 571
- Gooch crucible, 125
- Graduated cylinders, 245
- Gratings, 868
- Gravimetric analysis; *see also* name of element or method
 - calculations of, 140–46, 670–73
 - comparison of, with volumetric, 232
 - list of errors in, 211
 - methods of, table, 212
 - outline of process of, 11
 - reference works on, 210
- Gravimetric factor, 143
- Grease, 108, 252
- Gum arabic, for stabilizing suspended precipitates, 883, 885
- Haber process for NH_3 formation, 31
- Hafnium, EDTA titration, 584
- Half-reactions, 396
 - in balancing redox equations, 398
 - combination of, 807
 - in finding redox equivalent weight, 401
 - list of (TSP), 930

- Halide mixtures
 - argentimetric titration of, 760
 - indirect gravimetric analysis of, 671, 736
- Halides; *see* Bromide; Chloride; Iodide
- Halogens; *see also* Bromine; Chlorine; Iodine
 - determination of, in organic compounds, 302, 735, 759
- Heat of dissociation, 678
- Heating, 100
- Hexamethylenetetramine, in ammonia determination, 381
- Homogeneous precipitation, 719, 740
- Hooks, glass, 100, 115, 136
- Hot plate, electric, 100
- Humidity, relative, 683
- Hydrates
 - preparation of, 682
 - as primary standards, 682
 - solubility of, 707, 713 (Prob. S2)
 - vapor pressure of, 678–82, 683
- Hydration of ions and protons, 161, 316
- Hydrazine, volumetric determination of, 467, 471, 844
- Hydrazo compounds, titration of, 856, 857
- Hydrochloric acid
 - azeotropic primary standard, 795
 - composition of reagent, 913
 - as extractant for ores, 476, 482, 488
 - gravimetric determination of, 234
 - standard solution of, 241, 365
 - titration of, in presence of H_3PO_4 , 376
 - titration of, with standard base, 365
- Hydrofluoric acid
 - composition of reagent, 913
 - volatilization of silica by, 477, 691
- Hydrogen, gravimetric determination of, as H_2O , 212
- Hydrogen ion; *see* Acid-base entries; Acids; pH
- Hydrogen-oxygen reaction, 30
- Hydrogen peroxide
 - as preoxidant, 818, 824
 - reaction with ferrous ion, 814
 - reduction of, with arsenite, 844
 - volumetric determination of, 456, 467, 471, 844
- Hydrogen sulfide
 - as prereducer, 822
 - volumetric determination of, 467, 837
- Hydrolysis, 325; *see also* name of substance
 - effect on solubility product calculations, 709
 - of metal ions, 584, 769
- Hydrostat, 682
- Hydroxamic acid, determination of, 526
- Hydroxide; *see also* Bases; name of base
 - titration of, in presence of carbonate or bicarbonate, 795
- Hydroxylamine
 - in fatty acid determination, 526
 - formation of, in Zn reductor, 821
- 8-Hydroxyquinoline, 212, 523, 569–70, 855
- Hypohalites, determination of, 467, 735
- Hypoiodite, as error source in iodimetric methods, 462, 463
- Ignition, 100, 103, 128; *see also* Precipitates, ignition of
 - of inorganic compounds, 212, 690–92
- Indicator blank, 357
- Indicators; *see also* name of indicator
 - acid-base, 352, 778–83, 914, 928
 - adsorption, 286–89, 295, 756, 763, 914
 - argentimetric titration, 279–89, 754–58
 - external, 283, 451
 - fluorescent, 355, 782
 - function of, 11, 229
 - metal ion, 585–87
 - mixed, 355, 366, 782, 914
 - preparation of solutions of, 914
 - for redox titrations
 - with bromate, 853
 - with cerate, 469, 836
 - with dichromate, 472, 835
 - internal, 447, 833
 - with iodate, 843
 - iodimetric, 458–60, 914
 - permanganimetric, 452, 457, 837
 - with reducing solutions, 475, 855–57
 - for spectrophotometric titrations, 543, 587
 - transition of
 - acid-base, 353, 778–83, 928
 - metal ion, 585–87
 - redox, 447, 833
 - turbidity, 355, 782
- Indirect analysis
 - by difference, 145, 639
 - gravimetric, 671, 736
 - by loss in weight, 153, 155, 156, 690, 692
 - volumetric, 231, 456, 467, 471, 589, 844; *see also* name of method
- Indium
 - EDTA titration, 584
 - oxine precipitation, 570
- Induced reactions, 32, 812, 840, 841
- Inert-electrolyte effect, 171, 701, 708
- Infrared lamps, 102, 132
- Infrared spectrophotometry, 512, 873, 875
- Inorganic compounds, stability of, on ignition, 690–94

- Instrumental methods of analysis, 12, 537–55
- Intensity, 506, 511, 517
- Interferences; *see also name of analytical method*
 methods of removal of, 9, 523
 in spectrophotometry, 519–21, 523
- Iodate
 determination of, as AgI, 735
 titrations with, 452, 842
 volumetric determination of, 302, 467, 845
- Iodide; *see also* Iodine
 air-oxidation of, 462
 gravimetric determination of, 212, 735
 and triiodide equilibrium, 460
 volumetric determination of, 302, 456, 467, 471, 758, 760, 837, 840, 845
- Iodide-iodate reaction, 845
- Iodimetric titrations, 458, 842–51
- Iodine; *see also* Iodide
 adsorption of, on CuI, 490
 autodecomposition of, 462
 catalysis of arsenite-permanganate reaction by, 455
 determination of, in organic compounds, 735, 759
 oxidation states of, 458, 842
 primary standard, 440, 460, 464
 reaction of, with arsenite, 461, 849
 standard solution of, 460
 volumetric determination of, 467, 844
- Iodine monochloride, as catalyst, 455, 469, 843
- Iodine-thiosulfate titration, 463
- Iodoform, argentimetric titration of, 759
- Ion exchange, 740
- Ion product of water, 29, 317
- Ionic activity coefficients, 701, 921
- Ionic diameters, 702, 921
- Ionic strength, 28, 701
- Ionization and ionization constants
 of acids, 22, 29, 316, 319, 332, 335, 923, 925
 of amino acids, 336
 of amphiprotic substances, 335
 of bases, 22, 29, 316, 320, 335, 923, 925
 from electrochemical data, 421
 of 8-hydroxyquinoline, 336
 of salts, 22, 161, 769
 tables of, 923, 925
 theory, 316, 326, 769
 of water, 29, 317
- Ions
 adsorbed, 185–93
 counter, 187
 hydration of, 161, 316
- Iron; *see also* Ferric and Ferrous entries
 determination of, in ores, 476
 interference of, with Cu determination, 489
 prereduction of, 477, 820–22
 spectrophotometric determination of, 523
 spectrophotometric titration of, 543, 587–88
 volumetric determination of, 456, 467, 471, 472, 476, 841, 844, 856, 857
- Iron ores, determination of iron in, 476
- Iron wire, primary standard, 440, 470, 478, 855
- Irreversible indicators, 451, 853
- Irreversible reactions, 426
- Isomorphism
 of BaSO₄ and BaCrO₄, 224
 and coprecipitation, 199, 724
 of silver halides, 763
- Isotherm, adsorption, 684, 698 (Prob. S20)
- Jones reductor, 820
- Joule, 420
- Junction potentials, 424, 446, 550, 829
- Karl Fischer titration for water, 689
- Ketones, permanganometric titration of, 837
- Kjeldahl method for N as NH₃, 378
- Laboratory notebook, 67, 157, 216, 294, 367
- Laboratory operations; *see name of operation*
- Laboratory work, elementary; *see* Students, work of
- Lamps, infrared, 102, 132
- Langmuir adsorption equation, 698 (Prob. S20)
- Lanthanum, determination of, with permanganate, 456
- Lanthanum oxalate, contamination by, 723
- Leaching of samples, 9, 481
- Lead
 gravimetric determination of, 212, 570, 737
 interference of, in Cu determination, 489
 as prereducer, 821, 822
 volumetric determination of, 290, 456, 467, 584, 587, 759
- Lead chlorofluoride, 723, 759
- Lead dioxide
 as preoxidant, 474, 822
 titration of, with KIO₃, 844
- Lead ion, adsorption of, by CaSO₄, 191
- Lead sulfate, 212, 224, 737
 direct titration with EDTA, 589
- Le Châtelier's principle, 25, 162, 165

- Leveling, of strong acids and bases, 784
 Liebig titration (CN^- - Ag^+), 572
 Ligands, 561-62
 Light, properties and types of, 505-8;
 see also name of type
 Light absorption, mechanism of, 506,
 585, 756, 778
 Light source, for spectrophotometer, 867
 Limestone
 analysis of, 481, 590
 decomposition of, on heating, 482, 690
 Liter, definition of, 650
 Lithium, gravimetric determination
 of, 212
 Locker equipment for elementary
 work, 910
 Logarithms, 165, 901
 Long swings, weighing method of, 76,
 655
 Lubrication, 108, 252

 McBride titration of oxalate with
 permanganate, 484, 840
 Magnesium
 gravimetric determination of, 212, 570
 postprecipitation of, on CaC_2O_4 ,
 197, 483
 spectrophotometric titration of, 588
 volumetric determination of, 471, 582,
 584, 587, 590, 854
 Magnesium ammonium phosphate, 105,
 163, 213
 Magnesium oxalate, solubility of, 197
 Magnesium perchlorate, as desiccant,
 155, 687
 Magnesium pyrophosphate, 212
 Malaprade (periodate) reaction, 846
 Manganate, 837
 Manganese
 coprecipitation of, by CaC_2O_4 , 483
 oxidation states of, 453, 837-40
 precipitation with oxine, 570
 preoxidation of, 526, 818-20, 822-24
 spectrophotometric determination
 of, 526
 volumetric determination of, 456, 467,
 475, 584, 844, 856, 857
 Manganese dioxide, titration of, with
 KIO_3 , 844
 Manganous ion, as catalyst in oxalate-
 permanganate reaction, 839
 Mannitol in boric acid titration, 788
 Marcali-Rieman determination of N as
 NH_3 , 380
 Marking equipment, 133, 749
 Mass, definition of, 650
 Maximum error, of computed result, 57
 Mean
 comparison of two values of, 44, 45,
 622, 625
 confidence level of, 44, 622-28
 contrasted with median, 631, 633
 contrasted with μ , 44, 622
 definition of, 39
 estimation of μ from, 44, 622
 number of significant figures in, 639
 reliability of, 44, 618
 standard deviation of, 618
 Measurement; *see also name of method*
 or quantity
 analytical methods of, 6-14, 537-49
 general procedure in making a, 44
 rejection of a, 45, 632
 reporting the result of a, 41, 144
 of sample, 8
 of sought-for substance, 10
 uncertainty of a, 54
 Measurements, distribution of, 42,
 613-15
 Median, 631, 633
 Meniscus, reading the, 255
 Mercaptans, argentimetric titration
 of, 759
 Mercuric chloride
 in bromate titrations, 853
 as oxidant for Sn(II) , 477
 preparation of reagent, 913
 Mercuric ion, complexing of, 570-71,
 572, 576, 582, 853
 Mercuric oxide
 behavior of, on heating, 691
 primary standard, 794
 Mercuric sulfide, behavior of, on
 heating, 691
 Mercurous chloride, titration of, with
 iodate, 844
 Mercury
 amalgams, 820
 gravimetric determination of, 213,
 690, 733
 as prereducer, 822
 volumetric determination of, 456, 467,
 471, 572, 584, 844
 Metal ion indicators, 585, 593
 Metal ions, hydrolysis of, 584, 769
 Metathesis
 definition of, 230
 with Na_2CO_3 , 220, 739, 744
 (Probs. S3, S4)
 Methods of analysis; *see* Analytical
 methods
 Methyl orange, 345, 779, 782, 914, 928
 Methyl red, 355, 366, 688, 782, 914, 928
 Methyl sulfate, as homogeneous
 precipitant, 740
 Methylene blue, 834
 Micromethods of analysis, 8
 Micropipets, 245, 751
 Minerals; *see* Ores
 Minor constituents, 8, 638

- Mixed crystals, 199, 724, 763
Mixed indicators, 355, 366, 688, 782, 914
Mixtures; *see also name of method or substance*
 analysis of, by density measurement, 538
 analysis of, by physico-chemical methods, 12, 537-40
 halide, argentimetric titration of, 760
 indirect analysis of, 671, 736; *see also* Indirect analysis
 redox titration of, 452, 473, 823
 spectrophotometric analysis of, 519, 521, 525, 530, 872, 875
- Mohr pipet, 246
Mohr titration for chloride, 281, 303, 754
Mohr's salt, 440, 476
Moisture; *see* Water
Molar absorptivity, 511
Molar concentration, 21, 236
Mole, use of, in problems, 21, 140-43, 236
Mole per cent, 679
Molecular weights, 21, 140, *inside front cover*
- Molybdenum
 gravimetric determination of, 213, 570
 prereduction of, 822
 volumetric determination of, 456, 471, 823, 844, 857
- Monochromator, 510, 868
Morse-Blalock calibration bulbs, 750
- Mother liquor
 occlusion of, 201-5
 technique for removing, 117-30
- Muffle furnace, 101
Multiple equilibria, 327, 561-63, 769-75
Munroe crucible, 128
- National Bureau of Standards, 76, 256, 324, 439, 637, 653, 748, 941
- Nephelometry, 524, 884
Nernst equation, 406, 808
Neutral solution, 318
Neutralization; *see* Acid-base entries;
 Acids; Bases
- Nickel
 as catalyst for formate-permanganate reaction, 837
 gravimetric determination of, 213, 570
 preoxidation of, 819, 822
 spectrophotometric titration of, 542, 587
 titration of, 582, 584, 844
- Niobium, gravimetric determination of, 213, 570
- Nitrate; *see also* Nitric acid
 determination of, as NH_3 , 379, 821
 gasometric determination of, by reduction with Hg, 12
 removal of, by evaporation, 133
- Nitric acid; *see also* Nitrate
 composition of reagent, 913
 for extraction of copper ores, 488
 removal of N oxides from, 300, 302, 488
- Nitrite; *see also* Nitrogen oxides
 decolorization of permanganate by, 530
 for reduction of oxyhalogen salts, 735
 volumetric determination of, 456, 467, 471, 853
- Nitro compounds, titration of, 856, 857
- Nitrobenzene, in Volhard titration, 301-3
- Nitroferroin, 448, 469, 836
- Nitrogen
 determination of, as NH_3 , 378
 by Dumas method, 381
 fixation of, 30
- Nitrogen oxides; *see also* Nitrite
 as catalyzer for air-oxidation of iodide, 462
 removal of, 300, 302, 488
- p*-Nitrophenol, structure of, 779
- Nitroso compounds, titration of, 856, 857
- Nitrous acid, removal of, 300, 302, 488
- Nonaqueous titrations, 784
- Nonstoichiometrical methods, 10-13, 537-40
- Normal curve, 43, 613, 908, 909
- Normality, 21, 236, 401
- Notebook, laboratory, 67, 157, 216, 294, 367
- Nucleation, theory of, 716
- Nuclei, crystal, 178-84, 716-19
- Number of determinations
 performed in an analysis, 53
 and reliability of mean, 44, 618
- Occlusion, 151, 201-5
- Olefins, permanganimetric titration of, 837
- Ores
 chromium in, 474
 copper in, 488
 decomposition of, for analysis, 115, 474, 481, 739, 744 (Probs. S3, S4), 819
 iron in, 476
 limestone, calcium in, 481
 manganese in, 525
 mercury in, 690
 reporting composition of, 144, 481
 silica in, 476, 691
 sulfur in, 737, 740, 819
 tin in, 692

- Organic compounds; *see also name of compound*
 analysis of, for elements, 302, 735, 759, 818, 820
 ashing of, 818, 820
 determination of unsaturation in, 467, 837
 volumetric determination of, 456, 467, 759, 837, 852, 856, 857
- Organic materials; *see also name of material*
 determination of water in, 153–55, 688–89
 drying of, 153
 noninterference of, in titrations with KIO_3 , 845
 spectrophotometric determination of Mn in, 525
- Orthophenanthroline, 448, 469, 472, 479, 836, 914
- Oscillations, damped, 655
- Osmium tetroxide, as catalyzer for arsenite-cerate titration, 469
- Ostwald pipet, 750
- Ostwald process, nitrogen fixation, 30
- Ostwald ripening, 203, 706, 727
- Oven, electric, 101
- Oven-drying, 100
- Oversize balance, 153, 661
- Overvoltage, 424
- Oxalate
 as complexer for Al and Fe, 482, 789
 as precipitant for Ca, 481
 stability of, in aqueous solution, 839
 volumetric determination of, 456, 471, 853
- Oxalic acid, primary standard, 439, 793
- Oxidation number, 395–96, 401
- Oxidation-reduction, 395–98; *see also Redox entries*
 prior to analysis, 440, 818–24
- Oxidizing agents, 395–98; *see also name of agent*
 strong, 395–98, 527, 738, 818–20, 822–24
- Oxine, 212, 569, 570, 854
- Oxygen, determination of, in air, 467, 857
- Ozone
 iodimetric determination of, 467
 as preoxidant, 819, 822
- Palladium
 complexing by dithizone, 571
 precipitation by oxine, 570
- Paneth-Fajans-Hahn adsorption rules, 190–92
- Paper, filter; *see* Filter paper
- Parallax, 255
- Parr oxidation, 302, 735, 818
- Partial analysis, 7
- Particle size
 in nephelometry, 885
 of precipitates, 179, 183, 705, 716, 727
 and solubility, 705, 727
 in turbidimetry, 882
- Peptization, 185, 194, 219, 721
- Perchlorate, determination of, as AgCl , 735
- Perchloric acid
 in extraction of ores, 488
 fuming with, 133, 820
 as preoxidant, 474, 819, 822, 824
- Period of balance, 653
- Periodate
 determination of, as AgI , 735
 in determining organic compounds, 846
 in determining potassium, 848
 iodimetric determination of, 467
 as oxidant for Mn, 525, 527
 as preoxidant, 822
- Periodic acid; *see* Periodate
- Permanganate
 absorption curve of, 529
 oxidation of chloride by, 841
 as preoxidant, 474, 822
 stability of, in aqueous solution, 453
 standard solutions of, 453, 484, 837–41
 titrations with, 456–57, 481, 837–38
 volumetric determination of, 456, 467, 475, 844, 855–57
- Peroxide; *see* Hydrogen peroxide
- Persulfate
 decomposition of, by boiling, 527
 determination of, with permanganate, 456
 as preoxidant, 474, 527, 818, 822, 823
- pH, 317; *see also* Acid-base entries;
 Acids
 of acid-base indicator transition range, 353, 779–82, 928
 in automatic titrations, 778, 832
 as basis for automatic control, 546
 of buffers, 321–25
 control of, in spectrophotometry, 521
 effect of
 on BaSO_4 determination, 221–25
 on completeness of arsenite-iodine reaction, 461, 849
 on complexation, 563, 571
 on *E*, 408, 424, 447, 849
 on EDTA titrations, 579–82
 on metal ion indicators, 587
 on physiological reactions, 325, 409
 on redox indicator, 447, 833
 on solubility, 163, 482, 570
- pH meter
 for establishing end points, 350, 371–78, 778, 832

- glass electrode in, 828
- Phase diagrams, 676–82, 690
- 1,10-Phenanthroline, 448, 469, 472, 479, 836, 914
- Phenolphthalein, 345, 355, 363, 780, 914, 928
- Phenols, titration of, with KBrO_3 , 854
- Phosphate; *see also* Phosphoric acid
 - as complexer for Fe(III) , 528, 842
 - gravimetric determination of, 213
 - volumetric determination of, 290, 302, 362, 371–78, 456, 471, 589
- Phosphate mixtures
 - pH of, 333
 - titration of, 376, 797
- Phosphoric acid; *see also* Phosphate
 - composition of reagent, 913
 - titration of, with standard base, 371–78
 - titration curve of, 362, 375
- Phosphorus, determination of, in organic compounds, 735; *see also* Phosphate
- Phosphorus pentoxide, as desiccant, 686
- Photocells, for spectrophotometer, 522, 868
- Photometer, filter, 522
- Phthalic acid, titration curve of, 362
- Physiological reactions, dependence of, on pH, 325, 409
- Pipets; *see also* Volumetric apparatus
 - calibration of, 247, 263, 266, 269, 751
 - cleaning of, 248
 - drainage from, 258, 746
 - reading of meniscus in, 255
 - specifications and tolerances of, 245, 746
 - types of, 245
 - use of, 258, 266, 269, 748
- Platinized electrodes, 418, 828
- Platinum crucibles, 105, 128
- Polarity, of electrochemical cell, 416
- Polarization, 417, 424
- Policeman, rubber, 123
- Polyethylene bottles, 98, 123, 138, 359, 577, 592, 839
- Polymorphism, 704
- Polyprotic acids and bases, 332, 361, 370–78, 578, 792, 795
- Porcelain ware, stability of, 104, 131
- Postprecipitation, 197, 202–5, 481
- Potassium
 - gravimetric determination of, 213, 671, 848
 - volumetric determination of, 456, 471, 848
- Potassium acid phthalate
 - buffer solutions of, 324, 915
 - as primary standard for bases, 366, 785
 - titration of, 362, 365, 371
- Potassium chlorate; *see also* Chlorate
 - as preoxidant, 822
- Potassium chloride; *see also* Chloride
 - sample series of, with NaCl , 741
- Potassium chromate, indicator solution of, 282, 303, 914
- Potassium dichromate; *see* Dichromate
- Potassium hydroxide; *see also* Bases
 - as desiccant, 687
- Potassium perchlorate; *see also* Perchlorate
 - as weighing form for K, 213
- Potassium periodate; *see* Periodate
- Potassium permanganate; *see* Permanganate
- Potassium salts, primary standards
 - bitartrate, 793
 - bromate, 440, 464, 853
 - bromide, 292
 - chloride, 292, 741, 799
 - dichromate, 440, 464, 478, 856–57
 - ferricyanide, 440, 464, 850
 - ferrocyanide, 440, 470
 - fluotitanate, 855
 - iodate, 440, 464, 794, 842
 - iodide, 440, 840
 - thiocyanate, 292
- Potentials
 - asymmetry, 554, 829
 - electrode; *see* Single-electrode potentials
 - junction, 424, 446, 550, 829
 - transition, 448, 833
- Potentiometer, 419, 446, 550
- Potentiometric determination of chloride, 550, 895
- Potentiometric titrations, 445, 543, 827
 - acid-base, 371, 376
 - with cerate, 442, 469
 - of chloride with silver, 289, 831–32
 - with Cr(II) , 856
 - with EDTA, 582
 - with Fe(II) , 442, 475
 - of Fe(II) with dichromate, 473
 - of iodide with permanganate, 841
 - iodimetric, 460
 - of mixtures, 452, 473
 - of silver with chloride, 289, 831–32
 - with Ti(III) , 855
- Powers and roots, 15, 901
- Precipitates
 - aging of, 183, 189, 203, 705, 707, 727
 - contamination of; *see* Contamination of precipitates
 - crystalline, 178, 181–84, 717
 - digestion of, 117, 203, 728
 - filtration of, 117–30, 184
 - formation of, 178–84, 716–19
 - gravimetric, desirable properties of, 177

Precipitates—*Cont.*

- ignition and drying of, 103–6, 112, 211, 212, 219, 223; *see also* Ignition
- peptization of, 185, 194, 219, 721
- thermal stability of; *see* Thermal stability
- titration of, with EDTA, 589
- transfer of, 120–25, 128–30
- types of, 181–84
- washing of, 117–30, 171, 175 (Prob. 1), 211–13

Precipitation

- choice of precipitant and conditions for, 171, 177, 205
- completeness of, 117, 161, 163, 169
- effect of, on E , 408
- effect of, on equilibrium, 26
- homogeneous, 719, 740
- mechanism of, 178–84, 716–19
- rate of, 163, 178–84, 716–19
- for removal of interferences, 9
- techniques for, 116

Precipitation titrations

- argentimetric, 273–308, 754–63
- curves of, 275–79, 760
- end-point error in, 754
- equivalence-point indication in, 279, 754, 758
- limitations of, 289
- list of, 290, 758
- of mixtures, 760

- Precision, 37; *see also* Accuracy; Deviation; Errors; Standard deviation
- as check on accuracy, 53, 638
- improvement of, 44, 47, 618, 632
- of a measurement, 54
- related to deviation, 39
- related to spread of error curve, 44

- Preoxidation and prereduction, 440, 818–24; *see also* name of substance

Preservatives

- for KHP, 324, 915
- for $\text{Na}_2\text{S}_2\text{O}_3$, 464, 490
- for starch, 459, 914

Pressure-composition diagram

- for $\text{BaCl}_2\text{-H}_2\text{O}$, 679
- for $\text{CuSO}_4\text{-H}_2\text{O}$, 698

Pressure-temperature diagram

- for $\text{BaCl}_2\text{-H}_2\text{O}$, 681
- for CaCO_3 , 691
- for Ca(OH)_2 , 677
- for hydrates, 683
- for NaHCO_3 , 700 (Prob. S4)

Preventive solution, 842

Primary nuclei, 178–84, 716–19

Primary standards, 97, 233, 911; *see*

also name of substance

- acid-base, 793
- argentimetric, 292
- hydrates as, 682

redox, 439

Principal equilibrium, 328

Prisms, 868

Probability curves, 43, 613, 908–9

Projection-reading balance, 661

Properties, analytically useful, 12, 537–39

- Proportional error, 46, 50–51, 81, 83, 90, 144, 239, 636, 741; *see also* Titer method

Proton donors and acceptors, 316

Protons, hydration of, 316

Purification; *see* Reagents; name of method

Purity of reagents; *see* Reagents

Pyrex, stability of, 98, 130, 358

Pyridine, in Karl Fischer titration, 689

Pyrates, gravimetric determination of sulfur in, 737, 740, 819

Pyrolysis, 692

Pyrophosphate in KMnO_4 titrations, 838

Q test, for rejection of data, 633

Quadratic formula, 16

Qualitative analysis, 6

by spectrophotometry, 514, 875

Quantitative analysis, nature of, 1–14, 537; *see also* Analytical methods; name of method or substance

Quartz, in spectrophotometry, 868

Quartz crucibles, 104, 128, 131

Quartz-fiber microbalance, 663

Quinones, titration of, with Cr(II) or Ti(III) , 855–57

Radiant energy, 505–8

Random error; *see* Errors, random

Range, 39, 632

Rare earths, EDTA titration of, 584

Rate; *see also* name of analytical method, phenomenon, reacting substance

- of chemical reaction, 30–32, 424, 809–17

of color development or decolorization, 524

of complexation reactions, 565

of crystallization, 178–84, 704, 716–19

of decomposition of standard solution, 750; *see also* Solutions, standard

of electrode response, 828, 830

of indicator action, 283–84, 289, 778, 836

of precipitation, or dissolution, 163, 178–84, 716–19

of precipitation titrations, 283–84, 289

of preoxidation or prereduction, 823

of redox reactions, 424, 809–17

of thermal decomposition of solids, 115, 678, 692

in titration reactions, 230

- Reactions, chemical; *see names of substances or types*
- Reading card, use of, 255
- Reagents; *see also name of substance*
 color-forming, 509, 523, 542, 570, 588
 density and composition of, 911–13
 excess, use of, 117
 grades of, 97; *see also analytical method; name of substance*
 lists of, 911–15
 preparation and storage of, 98, 359, 749, 913–15
 primary standard; *see* Primary standards
 purity of, 97–99, 117, 491–92, 519, 875
 solutions of, 98, 359, 913–15
 testing of, 98–99, 117, 217, 222, 519
- Redox conjugate pair, 396
- Redox equations, balancing, 398
- Redox equilibria, 404–13, 421, 424;
see also names of substances
 activity effects in, 808
 and electrochemical cells; *see* Electrochemical cells
 elementary description of, 397, 404
 and equilibrium constants, 410, 421, 423, 808
 and half-reactions; *see* Half-reactions
 and single-electrode potentials; *see* Single-electrode potentials
 and tables of standard potentials, 397, 930
- Redox indicators; *see* Indicators, for redox titrations
- Redox normality, 401
- Redox potentials, tables of, 397, 930
- Redox reactions
 definition of, 395
 extent of, 397, 406, 424
 mechanism and kinetics, 424, 809–16
- Redox titer, 401
- Redox titrations, 438–52; *see also name of substance or type*
 calculation of E in, 441–45, 824
 curves of, 442, 543, 778, 824, 832
 elementary description of, 442
 establishing end point in, 445–52, 827–33
 of mixtures, 452, 473, 763, 823
 potentiometric; *see* Potentiometric titrations
 preoxidation or prereduction in, 818–24
 primary standards in; *see* Primary standards
 standard solutions used in, 439
 stoichiometry of, 401
- Reducing agent; *see also name of substance*
 definition of, 395
- Reduction; *see* Redox entries
- Reducers, 477, 820–23
- Reference electrodes, 445, 832
- Regeneration of desiccants, 687
- Rejection of data, procedure for, 45, 67, 633
- Relative error or deviation, 40
- Reliability
 of mean, 44, 618
 of standard deviation, 44, 615
- Reporting a result, 14, 41, 67, 144
- Reprecipitation, 129, 202, 204
- Response curves, for photocells, 869
- Rest point of a balance, 76–79, 88, 655–57
- Result
 of an analysis, checking accuracy of, 53, 636
 of an analysis, reporting, 14, 41, 67, 144
 computed, error of a, 14, 57, 640
- Rhodamine G, 758
- Rider; *see* Weights
- Rider balance, 74
- Rocks; *see* Ores
- Roots and powers, 15, 901
- Rubber bulb, for pipetting, 253
- Safety bottle, 127
- Salicylic acid, 543, 588
- Salt bridge, 415, 418, 447, 896
- Salts
 hydrates; *see* Hydrates
 hydrolysis of; *see* Hydrolysis
 solubility products of; *see* Solubility products
 titration of, 350, 362, 366, 370, 380
- Sample
 dissolution of, 9, 113, 205, 476, 481, 488
 drying of, 9, 103–9, 112, 153, 211, 686
 fusion of, 9, 115, 474, 481, 818
 history of, 8
 preparation of, 7, 8, 205, 235; *see also name of technique*
- Sample size, 8, 216, 670
- Samples
 standard, 53, 637
 transfer of, 112
 unknown, preparation of
 acid-base, 799
 argentimetric, 741, 763
 $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ -NaCl, 694
 NaCl-KCl, 741
 Na_2SO_4 -NaCl, 741
 rock and ore, 858
 use of solutions in, 764, 799
 weighing of, 9, 81, 109; *see also* Weighing
- Sampling, 8, 235, 300

- Scandium, oxine precipitation of, 570
 Schellbach buret, 247
 Schulze-Hardy rule, 192, 720
 Selected sample weights, 670
 Selectivity, 13; *see also* Spectrophotometry, selectivity in
 in prereduction, 823
 Selenium
 as catalyst for Kjeldahl digestion, 379
 determination of, 213, 456
 preoxidation of, 819
 Semi-micromethods of analysis, 8
 Sensitivity of analytical methods, 8;
 see also name of method
 Sensitivity of balance, 71, 88, 650, 661
 Separation
 with complexers, 569
 of sought-for substance, 7, 9
 Short swings, weighing method of, 79
 Sign conventions, for single-electrode
 potentials, 397, 409
 Significant-figure rule, 56, 61 (Prob. 2),
 639
 Silica
 determination of, 213, 691
 fusion of, with Na_2CO_3 , 476
 hydrous, contamination of, 691
 in limestone, 481-82
 precipitation of, by HCl , 476
 volatilization of, by HF , 477, 691
 Silica apparatus, chemical resistance of,
 130
 Silica crucibles, 104, 128, 130
 Silica gel, as desiccant, 686
 Silicate error, in acid-base titrations, 358
 Silicates, decomposition of, on ignition,
 482, 487
 Silicon tetrafluoride, in determination of
 silica, 477, 691
 Silver
 complexation by dithizone, 571
 gravimetric determination of, 213, 733
 volumetric determination of, 280, 284,
 289, 298, 572, 758, 831
 Silver bromide, solubility of, 742
 Silver chloride; *see also* Chloride
 contamination of, 204, 217-20, 296,
 299, 302, 306
 drying of, 219
 melting point of, 219
 photoreduction of, 218, 296
 precipitation of, 214
 solubility of, 162, 734
 stability of colloid of, 186, 194, 219,
 295
 supersolubility of, 706
 Silver chromate
 as indicator for Mohr titration, 281,
 303, 754
 solubility-product calculations for,
 164-70, 282, 304, 754
 Silver ion, as catalyst in persulfate
 oxidations, 818
 Silver nitrate
 primary standard, 291
 pyrolysis of, with thermobalance, 693
 reagent solution of, 913
 Silver reductor, 477, 821-23
 Silver salts, solubilities of, 296, 916
 Silver-copper alloy
 analysis of, with thermobalance, 693
 unknown sample series of, 763
 volumetric determination of Ag in,
 284, 298
 Simultaneous precipitation, 195, 723
 Single-electrode potentials
 accuracy of, 423
 calculation of equilibrium constants
 from, 410, 421, 423, 808
 concept of, 405
 correction of, for activities, 808
 dependence of, on concentration, 406
 effect of complexers and pH on, 408,
 424
 formal, 409, 930
 of indicators, 448
 measurement of, 417, 423
 and Nernst equation, 406, 808
 and reaction rate, 424
 standard, 407, 930
 table of, 397, 930
 in titrations, 441-47, 582, 824, 827-32
 Single-pan balance, 661
 Single swing, weighing method of, 656
 Sintered glass crucibles, 125, 215
 Slide rule, 16, 643, 901
 Sodium, determination of, 213, 456,
 471
 Sodium acetate, as buffer, 915
 Sodium arsenite; *see* Arsenic; Arsenious
 oxide; Arsenite
 Sodium bicarbonate
 as primary standard, 793
 thermal decomposition of, 152, 700
 (Prob. S4)
 Sodium bismuthate, as preoxidant, 441,
 819, 822
 Sodium carbonate
 fusion with, 476, 481, 487
 metathesis with, 220, 739, 744
 (Probs. S3, S4)
 as preservative for $\text{Na}_2\text{S}_2\text{O}_8$, 464, 490
 as primary standard, 366, 799
 titration of, 362-64, 365, 370
 Sodium chloride, as primary standard,
 292, 694, 741, 799
 Sodium diglycolate, as primary
 standard, 794

- Sodium diphenylamine sulfonate, 448, 472, 479, 835, 914
- Sodium ethylenediaminetetraacetate, as primary standard, 590
- Sodium formate, standard solution of, 837
- Sodium hydroxide
as desiccant, 687
reagent solution of, 913
standard solution of, 359, 366, 373
- Sodium magnesium uranyl acetate, 213
- Sodium oxalate, as primary standard, 439, 469, 484, 793, 839
- Sodium peroxide, 474, 735, 818
- Sodium sulfate, as primary standard, 741, 799
- Sodium thiosulfate, standard solution of, 464, 491, 850
- Sodium zinc uranyl acetate, 213
- Solid solutions, 151, 199–205, 723–27
- Sols, 193; *see also* Colloids
- Solubility, 160–64, 704–11
dependence on particle size, 705, 727
of electrolytes, 22
of 8-hydroxyquinolinates, 570
minimizing losses due to, 171
related to solubility product, 166–69, 174 (Prob. 6), 713 (Prob. S1)
- Solubility curves, 162, 169, 171, 180, 734, 742
- Solubility products
calculations involving, 165–70, 701–12
definition of, 28, 164
determination of, 166, 421–24
effect of inert electrolyte on, 171, 701
error-causing factors, 704–11
exponent of, 165
related to solubility, 166–69, 174 (Prob. 6), 713 (Prob. S1)
table of, 165, 916
- Solution, mechanism of, 160, 704–12
- Solutions
buffer, 321, 768
expressing composition of, 21, 235, 401, 406, 409
measurement of; *see name of apparatus or technique*
reagent; *see* Reagents
solid, 151, 199–205, 723–27
standard, 11, 233, 439
concentration range of, 233
primary; *see* Primary standards for spectrophotometry, 889
standardization of, 233, 749; *see also* Standardization
storage of, 98, 359, 749, 914–15
- Solvent extraction, 9; *see also names of substances*
- Solvents
coagulation of colloids by, 720
effect of, on adsorption, 192
effect of, on solubility, 161, 171, 737, 848
for samples; *see* Sample, dissolution of
- Specific gravity, of reagents, 913
- Specific gravity balance, 669 (Prob. S11)
- Specific surface, 188
- Specifications
for volumetric apparatus, 748
for weights, 75, 653
- Spectrophotometers, 510, 512, 522, 867, 881
- Spectrophotometric titrations, 541, 587
- Spectrophotometry, 505–31, 867–89
for analysis of mixtures, 519, 521, 872, 875
blank in, 519
chemical processes used in, 522
CO₂ determination by, 547
color development in, 523, 570
compared with other analytical methods, 509
high-precision, 876–82
importance of, 13, 509
interferences in, 519–21
measurement of transmittance by; *see* Transmittance
optimum absorbance in, 519, 876
pH control in, 521
qualitative analysis by, 514, 570, 875
quantitative analysis by, 514; *see also name of substance*
selection of wavelength range in, 514
selectivity in, 509, 514, 519, 521, 524, 873, 875
sources of errors in, 518, 530, 876
unstable systems in, 520, 524, 883–87
and the working curve, 515
- Spectroscopic analysis, 13, 539
- Spectrum
of incandescent source, 867
infrared, 512, 873, 875
regions of the electromagnetic, 506
visible, 507
- Spot plate, 284
- Squeeze bottle, 123
- Stability constants, 561, 566, 567
- Standard addition, 636
- Standard deviation, 39, 44, 615
comparison of s and σ , 44, 45, 628
comparison of two values of s , 45, 629
of a computed result, 640–43
of the difference between two means, 625
distribution of s , 45, 615, 628
estimation of s from range, 632
estimation of σ from s , 45, 615

- Standard deviation—*Cont.*
 of the mean, 618
 pooled, 627
 and spread of the error curve, 44, 613
- Standard electrodes, 418, 832
- Standard potentials; *see* Single-electrode potentials
- Standard samples, 53, 637
- Standard solutions; *see* Solutions, standard
- Standard state, 407
- Standards, primary, 97, 233, 911; *see also* Primary standards
- Stannic iodide, 692; *see also* Tin
- Stannic oxide, 692; *see also* Tin
- Stannous chloride, 473, 477, 822, 915; *see also* Tin
- Starch indicator, 451, 458, 841, 843, 914
- Statistical tests, 45, 620–34; *see also* Mean; Standard deviation
- Steel
 determination of chromium in, 474, 530
 determination of Mn in, 526
 determination of sulfur in, 739
 minor components in, 530
- Stirring techniques, 116, 372
- Stoichiometrical and nonstoichiometrical methods, 10–13, 537
- Stoichiometry in analytical calculations, 11, 21, 140–44, 235–42, 401, 573
- Stopcocks
 cleaning and greasing of, 251
- Teflon, 252
- Storage of reagents and standard solutions, 98, 359, 749, 914–15
- Strontium, determination of, 213, 456, 584, 737
- Strontium sulfate, weighing form of, 213, 737
- Student's *t*, 622, 626
- Students
 work of, grading, 634
 work of, suggestions for, 1–5, 52, 63–69, 96, 634
 unknown samples for; *see* Samples, unknown
- Sublimation, purification by, 439, 440
- Submicromethods of analysis, 8
- Substitution, weighing by, 82, 89, 267, 658
- Sugars, volumetric determination of, 837, 846
- Sulfamic acid, primary standard, 794
- Sulfate, gravimetric determination of, 206, 213, 221, 737–41, 744 (Prob. S3); *see also* Sulfuric acid
- Sulfates
 thermal stability of, 692
 turbidimetric determination of, 884
 volumetric determination of, 290, 589
- Sulfides; *see also* Sulfur
 determination of, 467, 737, 759, 837, 844
 postprecipitation of, 199
- Sulfite, determination of, 467, 738, 837; *see also* Sulfur dioxide
- Sulfur; *see also* Sulfide
 determination of, 213, 221, 290, 538, 735, 737–41, 744 (Prob. S3), 819, 844, 884
 preoxidation of, 819
- Sulfur dioxide, as prereducer, 735, 822; *see also* Sulfite
- Sulfuric acid; *see also* Sulfate
 azeotropic primary standard, 795
 composition of reagent, 913
 concentrated, as desiccant, 688
 determination of, by specific gravity, 538
 fuming with, 133, 488, 692
 titration curve of, 362–63
- Superoxol, 818
- Supersaturation, 179–83, 197, 716
- Supersolubility of small particles, 180, 727
- Surface-exchange adsorption, 707
- Surface tension, 706
- Systematic schemes, of quantitative analysis, 9
- t*, as multiplier for confidence limits, 622, 626
- Table of standard potentials, 397, 930
- Tantalum, gravimetric determination of, 213
- Tare, 82, 267, 660, 670
- Tartrate, as complexer for Fe(III), 225
- Techniques; *see name of operation or apparatus*
- Teflon stopcocks, 252
- Tellurium
 preoxidation of, 819
 volumetric determination of, 456, 471
- Temperature
 estimated from color, 100
 maximum, attainable with heat sources, 100
- Tests
 chemical; *see* Reagents
 statistical, 45, 620–34; *see also* Mean; Standard deviation
- Tetrathionate, 458, 464, 844
- Thallium, determination of, 471, 570, 584, 844, 853
- Thermal decomposition, analysis by, 152–57, 690–94
- Thermal stability; *see also name of compound*
 of crucibles, 104, 115, 128, 131

- of hydrates and inorganic compounds, 150-57, 212, 676-82, 690-94
- of precipitates, 103, 118, 212
- Thermobalance, 692
- Thermometric titrations, 543
- Thiocyanate
 - as complexer for Hg, Au, Cu, 571
 - determination of, 291, 302, 306, 734, 844
 - ferric ion as indicator for, 284, 298-303, 572
 - as indicator for Fe(III), 856
 - in iodimetric determination of Cu, 490
 - in spectrophotometric determination of Fe(III), 523
 - standard solution of, 291
 - in Volhard titration, 284, 298-303, 572
- Thiosulfate
 - gravimetric determination of, 738
 - reaction of, with iodine, 463
 - reaction of, with strong oxidants, 465
 - standard solution of, 464, 491, 850
 - volumetric determination of, 467, 471, 844
- Thorium, determination of, 290, 471, 570, 846
- Thymol, as mold preventative, 324, 915
- Tin; *see also* Stannic and Stannous entries
 - gravimetric determination of, 213, 692
 - volumetric determination of, 456, 467, 471, 589, 844, 855-57
- Titanium
 - in iron ore analysis, 477
 - in limestone analysis for Ca, 481-83
 - precipitation by oxine, 570
 - prereduction of, 477, 821-23
 - volumetric determination of, 456, 471, 584, 857
- Titanous chloride, titrations with, 452, 855
- Titer method, 238, 401; *see also* Proportional error
 - in determination of Cu in ore, 492
 - in determination of Fe in ore, 479
 - in Mohr titration for Cl, 303
 - in titration of H_3PO_4 , 374, 378
- Titration curves
 - acid-base, 343-51, 361-65, 369, 375, 781, 784-92
 - with EDTA and complexers, 574, 579
 - experimental measurement of, 289, 350, 371-78, 445, 540, 582-85, 778, 827, 832
 - instrumental, 289, 540, 778, 832
 - landmarks on, 348, 365
 - polyprotic acid, 361
 - precipitation, 273-79, 760
 - recorded, 778
 - redox, 442, 543, 778, 824, 832
- Titration; *see also* Volumetric analysis; *name of sought-for or standard substance*
 - acid-base, 343-85; *see also* Acid-base titrations
 - back; *see* Back titration
 - chronopotentiometric, 543
 - comparison of, with gravimetric analysis, 232
 - complexation, 571-94
 - definition, 11
 - with EDTA, 574-94
 - nonaqueous, 784
 - potentiometric, 445, 543, 827; *see also* Potentiometric titrations
 - precipitation, 273-308; *see also* Precipitation titrations
 - redox, 438-52; *see also* Redox titrations
 - spectrophotometric, 541, 587
 - techniques for performing, 258-61, 589
- Tolerances; *see name of apparatus*
- Trace methods of analysis, 8, 509, 550, 570
- Transition of indicators
 - acid-base, 353, 778-83, 928
 - metal, 585-87
 - redox, 447, 883
- Transmittance, 511
 - when absorptivity varies with wavelength, 871
 - factors affecting, 513, 518, 873
 - measurement of, 516, 527
 - optimum, 519, 876
 - for two absorbing solutes, 872-75
- Transmittance curves, 512, 521, 529, 876
- Triiodide, 460
- Tris (hydroxymethyl) aminomethane, 794
- Tungsten
 - determination of, with permanganate, 456
 - gravimetric determination of, 213, 570
 - prereduction of, 822
- Turbidimetry, 524, 882
- Turbidity indicators, 355, 782
- Ultramicrobalance, 664
- Ultramicromethods of analysis, 8
- Uncertainty, of an experimental quantity, 54
- Unsaturation in organic compounds, determination of, 467, 837
- Uranium
 - fluorimetric determination of, 887
 - precipitation by oxine, 570
 - prereduction of, 822
 - volumetric determination of, 456, 471, 584

- Uranyl ion, as external precipitation indicator, 283
- Urea, in removal of N oxides, 488
- Vanadium
 in iron ore analysis, 477
 precipitation by oxine, 570
 preoxidation and prereduction of, 818-22
 volumetric determination of, 456, 467, 471, 584, 844, 857
- Vapor pressure
 diagrams, 676-85, 691, 698, 700
 of droplets, 699 (Prob. S21), 706
 of hydrates, 678-83
- Vernier scale, 86
- Volatilization, for removal of interferences, 9, 133
- Volatilization methods of analysis, 150-57, 690-94
- Volhard titration, 284, 298, 301, 838
- Voltage of electrochemical cells, 416-19, 445, 827-33
- Voltmeter, vacuum tube, 419, 830
- Volumetric analysis, 11, 229-42
 calculations of, 11, 235-42
 comparison of, with gravimetric, 232
 direct and indirect methods, 231
 general procedure of, 11, 233
 reactions suitable for, 229, 289, 438
 standard solutions in, 11, 233, 439;
see also Solutions, standard
 types of reactions used in, 230-32
- Volumetric apparatus, 245; *see also* *name of equipment or technique*
 calibration of, 263, 266-69, 748, 751
 effect of temperature on, 251, 264
 errors in, 49, 261-66
- Volumetric techniques; *see also* *name of equipment or technique*
 marking, 133, 749
 measuring odd volumes by, 748
- von Weimarn precipitation of BaSO_4 , 183
- Vycor, chemical resistance of, 130
- Walden reductor, 477, 820-23
- Wash bottles, 138
- Washing, 121-25, 129, 171, 175 (Prob. 1), 202
- Water; *see also* Dissolution; Drying;
 Evaporation; Hydrates; Hydrolysis;
 Washing
 adsorption of, 682-85
 determination of, 152-57, 688
 distilled, as reagent, 99, 117, 217, 366, 519
 ion product of, 29, 317
- leveling effect of, 784
 rate of oxidation or reduction of, 425, 855, 856
 removal of CO_2 from, 99, 366; *see also* Carbonate error
 in solids, 150, 676-88
 vapor pressure of, 676-88
- Watt-seconds, 420
- Wavelength and color, 507
- Weighing
 containers for, 110
 double, 83, 657
 errors in, 49, 76, 79, 85-87, 89-91, 654, 657-60
 methods of, 76-79, 655-57
 by substitution, 82, 89, 267, 658
 techniques of, 109-13
- Weighing forms of precipitates, 144, 212
- Weight
 achieving constant, 112
 in air, contrasted with true weight, 83, 659
 compared with mass, 649
 equivalent, 237, 401
- Weight buret, 247
- Weights
 calibration or checking of, 49, 75, 83, 89-91, 657
 chain, 84, 88, 90
 description and use of, 75, 86, 653
 errors in, 83
 maintenance and repair of, 666
 rider, 75, 88-91, 655
 tolerances and specifications for, 75, 654
- Wet ashing, 636, 820
- Winkler titration of NH_3 , 380
- Witte plate, 126
- Working curves, 515, 528, 539, 834, 885, 886, 890 (Ques. S9-S11)
- X rays, 506, 509
- Xanthates, argentimetric titration of, 759
- Xylenol orange, 591
- z, multiplier for confidence limits, 622, 626
- Zimmerman-Reinhardt method, 842
- Zinc
 gravimetric determination of, 213, 570
 as prereducer, 477, 820-23
 volumetric determination of, 283, 290, 456, 467, 471, 575, 584, 758, 844
- Zinc sulfide, postprecipitation of, on Bi_2S_3 , 198
- Zirconium, determination of, 213, 570, 584

